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a computational chemistry approach

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Solution Manual to

Molecular Electromagnetism
A Computational Chemistry Approach

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Preface

Three years are gone since the first edition of the book has been published and at least four classes of students at the Department of Chemistry, University of Copenhagen, have tried to solve the exercises. Two classes, in particular, have been very dedicated and could be convinced to help me with finally finishing the solution manual. I am extremely thankful for their input and dedication and happy to share the authorship of the solution manual with them.

While writing the solution manual we found of course several errors in the book. All the corrections to these errors and errors, that I might find in the future in the book or the solution manual, will be collected on my blogpost for the book at: http://molecularelectromagnetism.blogspot.dk

Stephan P. A. Sauer
Copenhagen, February 2015

Contents

Solutions to Chapter 2

2.1 We start by inserting the product trial solution for the time-dependent wavefunction, Eq. (2.4), in the time-dependent Schrödinger equation, Eq. (2.3)

$$\hat{H}^{(0)}_{nuc,e}\ |\Phi^{(0)}(\vec{\boldsymbol{R}},\vec{\boldsymbol{r}})\ \vartheta(t)\rangle = \imath\hbar\frac{\partial}{\partial t}\ |\Phi^{(0)}(\vec{\boldsymbol{R}},\vec{\boldsymbol{r}})\ \vartheta(t)\rangle$$

which can be rearranged to

$$\frac{1}{\Phi^{(0)}(\vec{\boldsymbol{R}},\vec{\boldsymbol{r}})}\hat{H}^{(0)}_{nuc,e}\ |\Phi^{(0)}(\vec{\boldsymbol{R}},\vec{\boldsymbol{r}})\rangle = \frac{\imath\hbar}{\vartheta(t)}\frac{\partial}{\partial t}\ |\vartheta(t)\rangle$$

The left hand side depends now only on spatial coordinates, whereas the right hand side depends only on time. Because both sides are equal for all values of the variables they must be constant. We call the constant $E^{(0)}$ and obtain two equations

$$\frac{1}{\Phi^{(0)}(\vec{\boldsymbol{R}},\vec{\boldsymbol{r}})}\hat{H}^{(0)}_{nuc,e}\ |\Phi^{(0)}(\vec{\boldsymbol{R}},\vec{\boldsymbol{r}})\rangle = E^{(0)}$$

and

$$E^{(0)} = \frac{\imath\hbar}{\vartheta(t)}\frac{\partial}{\partial t}\ |\vartheta(t)\rangle$$

which can be rewritten as

$$\hat{H}^{(0)}_{nuc,e}\ |\Phi^{(0)}(\vec{\boldsymbol{R}},\vec{\boldsymbol{r}})\rangle = E^{(0)}|\Phi^{(0)}(\vec{\boldsymbol{R}},\vec{\boldsymbol{r}})\rangle$$

and

$$\frac{\partial}{\partial t}\ |\vartheta(t)\rangle = -\frac{\imath}{\hbar}E^{(0)}\vartheta(t)$$

The first equation is the time-independent Schrödinger equation, Eq. (2.5), whereas the latter is the eigenvalue equation for the time-dependent phase factor $\vartheta(t)$, with the solution

$$\vartheta(t) = e^{\frac{-\imath}{\hbar}E^{(0)}t}$$

2.2 When we insert the trial-solution $\Phi^{(0)}_{n,vJ}(\vec{\boldsymbol{R}},\vec{\boldsymbol{r}}) = \Psi^{(0)}_n(\vec{\boldsymbol{r}};\vec{\boldsymbol{R}})\ \Theta^{(0)}_{v,J}(\vec{\boldsymbol{R}})$, Eq. (2.11), in the total time-independent Schrödinger equation, Eq. (2.5), we obtain

$$\Theta^{(0)}_{v,J}\left\{\frac{1}{2m_e}\sum_i^N \hat{\vec{p}}_i^{\,2} + \frac{e^2}{4\pi\epsilon_0}\sum_{i<j}\frac{1}{|\vec{r}_i-\vec{r}_j|} - \frac{e^2}{4\pi\epsilon_0}\sum_{iK}^{NM}\frac{Z_K}{|\vec{r}_i-\vec{R}_K|}\right.$$
$$\left.+\frac{e^2}{4\pi\epsilon_0}\sum_{K<L}\frac{Z_K Z_L}{|\vec{R}_K-\vec{R}_L|}\right\}\Psi^{(0)}_n$$
$$+\ \Psi^{(0)}_n\frac{1}{2}\sum_K^M\frac{\hat{\vec{p}}_K^{\,2}}{m_K}\Theta^{(0)}_{v,J} +\ \Theta^{(0)}_{v,J}\frac{1}{2}\sum_K^M\frac{\hat{\vec{p}}_K^{\,2}}{m_K}\Psi^{(0)}_n + \sum_K^M\frac{1}{m_K}(\hat{\vec{p}}_K\Psi^{(0)}_n)\cdot(\hat{\vec{p}}_K\Theta^{(0)}_{v,J})$$
$$= E^{(0)}_{n,v,J}\Psi^{(0)}_n\ \Theta^{(0)}_{v,J}$$

Using that $\Psi^{(0)}_n(\vec{\boldsymbol{r}};\vec{\boldsymbol{R}})$ is the solution of the electronic Schrödinger equation (including the nuclear repulsion), Eq. (2.10), we can rewrite the first parenthesis of the left hand side as $E^{(0)}_n(\vec{\boldsymbol{R}})\ \Psi^{(0)}_n(\vec{\boldsymbol{r}};\vec{\boldsymbol{R}})$ and combine it with the second parenthesis of the left hand side

$$\Psi^{(0)}_n\left\{\frac{1}{2}\sum_K^M\frac{\hat{\vec{p}}_K^{\,2}}{m_K} + E^{(0)}_n(\vec{R})\right\}\Theta^{(0)}_{v,J}$$
$$+\ \Theta^{(0)}_{v,J}\frac{1}{2}\sum_K^M\frac{\hat{\vec{p}}_K^{\,2}}{m_K}\Psi^{(0)}_n + \sum_K^M\frac{1}{m_K}(\hat{\vec{p}}_K\Psi^{(0)}_n)\cdot(\hat{\vec{p}}_K\Theta^{(0)}_{v,J}) = E^{(0)}_{n,v,J}\Psi^{(0)}_n\ \Theta^{(0)}_{v,J}$$

Comparison with the nuclear Schrödinger equation, Eq. (2.12), shows that the terms which are neglected in the Born-Oppenheimer approximation are given as

$$\Theta^{(0)}_{v,J}\frac{1}{2}\sum_K^M\frac{\hat{\vec{p}}_K^{\,2}}{m_K}\Psi^{(0)}_n + \sum_K^M\frac{1}{m_K}(\hat{\vec{p}}_K\Psi^{(0)}_n)\cdot(\hat{\vec{p}}_K\Theta^{(0)}_{v,J})$$

They involve the first and second derivative of the electronic wavefunction with respect to the nuclear coordinates weighted by the corresponding nuclear masse m_K.

2.3 Starting from

$$\frac{\partial\rho^{el}(\vec{r}_1,t)}{\partial t} = -eN\frac{\partial}{\partial t}\int_{\vec{r}_2}\cdots\int_{\vec{r}_N}\left|\Psi^{(0)}_k(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N,t)\right|^2\ d\vec{r}_2\cdots d\vec{r}_N$$

we take the time-derivative of the probability density

$$\frac{\partial\rho^{el}(\vec{r}_1,t)}{\partial t} = -eN\int_{\vec{r}_2}\cdots\int_{\vec{r}_N}\left\{\frac{\partial\Psi^{(0)*}_k(\{\vec{r}_i\},t)}{\partial t}\Psi^{(0)}_k(\{\vec{r}_i\},t)\right.$$
$$\left.+\Psi^{(0)*}_k(\{\vec{r}_i\},t)\frac{\partial\Psi^{(0)}_k(\{\vec{r}_i\},t)}{\partial t}\right\}\ d\vec{r}_2\cdots d\vec{r}_N$$

The time derivative of the wavefunction and its complex conjugate is given by the time-dependent Schrödinger equation Eq. (2.13) leading to

$$\begin{aligned}\frac{\partial \rho^{el}(\vec{r}_1,t)}{\partial t} = -\frac{\imath e N}{2 m_e \hbar} \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Big\{ & \Psi_k^{(0)}(\{\vec{r}_i\},t) \hat{H}^{(0)} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \\ & - \Psi_k^{(0)*}(\{\vec{r}_i\},t) \hat{H}^{(0)} \Psi_k^{(0)}(\{\vec{r}_i\},t) \Big\} \; d\vec{r}_2 \cdots d\vec{r}_N\end{aligned}$$

All potential energy terms in the Hamiltonian are multiplicative operators and can therefore be moved in front of the product of the two wavefunctions. Consequently these contributions cancel and we are left with the kinetic energy terms

$$\begin{aligned}\frac{\partial \rho^{el}(\vec{r}_1,t)}{\partial t} = -\frac{\imath e N}{2 m_e \hbar} \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Bigg\{ & \Psi_k^{(0)}(\{\vec{r}_i\},t) \sum_{i=1}^{N} \hat{\vec{p}}_i^{\,2} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \\ & - \Psi_k^{(0)*}(\{\vec{r}_i\},t) \sum_{i=1}^{N} \hat{\vec{p}}_i^{\,2} \Psi_k^{(0)}(\{\vec{r}_i\},t) \Bigg\} \; d\vec{r}_2 \cdots d\vec{r}_N\end{aligned}$$

2.4 We start by rewriting the second part of the integral in Eq. (2.26) in the following way

$$\begin{aligned}& \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \sum_{i=1}^{N} \hat{\vec{p}}_i^{\,2} \Psi_k^{(0)}(\{\vec{r}_i\},t) \; d\vec{r}_2 \cdots d\vec{r}_N \\ = & \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \hat{\vec{p}}_1^{\,2} \Psi_k^{(0)}(\{\vec{r}_i\},t) \; d\vec{r}_2 \cdots d\vec{r}_N \\ & + \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \sum_{i=2}^{N} \hat{\vec{p}}_i^{\,2} \Psi_k^{(0)}(\{\vec{r}_i\},t) \; d\vec{r}_2 \cdots d\vec{r}_N\end{aligned}$$

and correspondingly for the first part

$$\begin{aligned}& \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)}(\{\vec{r}_i\},t) \sum_{i=1}^{N} \hat{\vec{p}}_i^{\,2} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \; d\vec{r}_2 \cdots d\vec{r}_N \\ = & \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)}(\{\vec{r}_i\},t) \hat{\vec{p}}_1^{\,2} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \; d\vec{r}_2 \cdots d\vec{r}_N \\ & + \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)}(\{\vec{r}_i\},t) \sum_{i=2}^{N} \hat{\vec{p}}_i^{\,2} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \; d\vec{r}_2 \cdots d\vec{r}_N \\ = & \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)}(\{\vec{r}_i\},t) \hat{\vec{p}}_1^{\,2} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \; d\vec{r}_2 \cdots d\vec{r}_N \\ & + \left(\int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \sum_{i=2}^{N} \hat{\vec{p}}_i^{\,2} \Psi_k^{(0)}(\{\vec{r}_i\},t) \; d\vec{r}_2 \cdots d\vec{r}_N \right)^*\end{aligned}$$

where the last equal sign is a consequence of the fact that for a given value of $\vec{r}_1$ the second integral is just an integral over an hermitian operator for a $N-1$ electron system. The expectation value of $\sum_{i=2}^{N} \hat{\vec{p}}_i^{\,2}$, however, is real and we can therefore write it as

$$
\begin{aligned}
&\int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)}(\{\vec{r}_i\},t) \sum_{i=1}^{N} \hat{\vec{p}}_i^{\,2} \Psi_k^{(0)*}(\{\vec{r}_i\},t)\ d\vec{r}_2 \cdots d\vec{r}_N \\
=&\int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)}(\{\vec{r}_i\},t) \hat{\vec{p}}_1^{\,2} \Psi_k^{(0)*}(\{\vec{r}_i\},t)\ d\vec{r}_2 \cdots d\vec{r}_N \\
&+ \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \sum_{i=2}^{N} \hat{\vec{p}}_i^{\,2} \Psi_k^{(0)}(\{\vec{r}_i\},t)\ d\vec{r}_2 \cdots d\vec{r}_N
\end{aligned}
$$

which is the same integral over the $\sum_{i=2}^{N} \hat{\vec{p}}_i^{\,2}$ as in the second contribution to Eq. (2.26). These two contributions cancel therefore and we are left with

$$
\begin{aligned}
\frac{\partial \rho^{el}(\vec{r}_1,t)}{\partial t} = \frac{-\imath e N}{2 m_e \hbar} \int_{\vec{r}_2} \cdots \int_{\vec{r}_N} &\Big\{ \Psi_k^{(0)}(\{\vec{r}_i\},t) \hat{\vec{p}}_1^{\,2} \Psi_k^{(0)*}(\{\vec{r}_i\},t) \\
&- \Psi_k^{(0)*}(\{\vec{r}_i\},t) \hat{\vec{p}}_1^{\,2} \Psi_k^{(0)}(\{\vec{r}_i\},t) \Big\}\ d\vec{r}_2 \cdots d\vec{r}_N
\end{aligned}
$$

2.5 We have to show that the change of the scalar and vector potentials according to

$$
\begin{aligned}
\phi^{\,\mathcal{E}}(\vec{r},t) &\to \phi^{\,\mathcal{E}'}(\vec{r},t) = \phi^{\,\mathcal{E}}(\vec{r},t) - \frac{\partial \chi(\vec{r},t)}{\partial t} \\
\vec{A}^{\mathcal{B}}(\vec{r},t) &\to \vec{A}^{\mathcal{B}'}(\vec{r},t) = \vec{A}^{\mathcal{B}}(\vec{r},t) + \vec{\nabla}\chi(\vec{r},t)
\end{aligned}
$$

will leave the electric field $\vec{\mathcal{E}}(\vec{r},t)$ and the magnetic induction $\vec{\mathcal{B}}(\vec{r},t)$ unchanged. Inserting the gauge transformed potentials in the expressions for the fields, Eqs. (2.33) and (2.34) gives

$$
\begin{aligned}
\vec{\mathcal{E}}\,'(\vec{r},t) &= -\vec{\nabla}\phi^{\mathcal{E}'}(\vec{r},t) - \frac{\partial \vec{A}^{\mathcal{B}'}(\vec{r},t)}{\partial t} \\
&= -\vec{\nabla}\left(\phi^{\,\mathcal{E}}(\vec{r},t) - \frac{\partial \chi(\vec{r},t)}{\partial t}\right) - \frac{\partial\left(\vec{A}^{\mathcal{B}}(\vec{r},t) + \vec{\nabla}\chi(\vec{r},t)\right)}{\partial t} \\
\vec{\mathcal{B}}\,'(\vec{r},t) &= \vec{\nabla} \times \vec{A}^{\mathcal{B}'}(\vec{r},t) \\
&= \vec{\nabla} \times \left(\vec{A}^{\mathcal{B}}(\vec{r},t) + \vec{\nabla}\chi(\vec{r},t)\right)
\end{aligned}
$$

If we now expand the gradients and curls we get

$$
\begin{aligned}
\vec{\mathcal{E}}\,'(\vec{r},t) &= -\vec{\nabla}\phi^{\,\mathcal{E}}(\vec{r},t) + \vec{\nabla}\frac{\partial \chi(\vec{r},t)}{\partial t} - \frac{\partial \vec{A}^{\mathcal{B}}(\vec{r},t)}{\partial t} - \frac{\partial \vec{\nabla}\chi(\vec{r},t)}{\partial t} = \vec{\mathcal{E}}(\vec{r},t) \\
\vec{\mathcal{B}}\,'(\vec{r},t) &= \vec{\nabla} \times \vec{A}^{\mathcal{B}}(\vec{r},t) + \vec{\nabla} \times \vec{\nabla}\chi(\vec{r},t) = \vec{\mathcal{B}}(\vec{r},t)
\end{aligned}
$$

because the curl of a gradient vanishes, $\vec{\nabla} \times \vec{\nabla}\chi(\vec{r},t) = 0$, and the partial derivatives with respect to time and spatial coordinates can be interchanged,

$$\vec{\nabla}\frac{\partial\chi(\vec{r},t)}{\partial t} = \frac{\partial\vec{\nabla}\chi(\vec{r},t)}{\partial t}$$

2.6 The task is to show that on insertion of the Lagrangian

$$\mathcal{L}(\vec{r},\vec{v},t) = \frac{m_e\vec{v}^{\,2}}{2} + e\,\phi^{\,\mathcal{E}}(\vec{r},t) - e\,\vec{v}\cdot\vec{A}^{\,\mathcal{B}}(\vec{r},t)$$

in the (Euler)-Lagrange equations

$$\frac{d}{dt}\left[\frac{\partial\mathcal{L}}{\partial v_x}\right] - \frac{\partial\mathcal{L}}{\partial r_x} = 0$$

we can recover the Newton's second law, Eq. (2.50), where the force $\vec{F}$ is the Lorentz force, Eq. (2.43), *i.e.* we should obtain Eq. (2.51). The (Euler)-Lagrange equations are a set of equations, one for each coordinate. Here we will restrict ourselves to only one coordinate which we choose to be the cartesian coordinate x. Therefore we should recover the equation relating the x component of the velocity to the x component of the Lorentz force.

Let us start with the second term in the (Euler)-Lagrange equations, Eq. (2.49). For the x-component we obtain

$$\frac{\partial\mathcal{L}}{\partial r_x} = e\frac{\partial\phi^{\,\mathcal{E}}(\vec{r},t)}{\partial r_x} - e\left(v_x\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_x} + v_y\frac{\partial A_y^{\mathcal{B}}(\vec{r},t)}{\partial r_x} + v_z\frac{\partial A_z^{\mathcal{B}}(\vec{r},t)}{\partial r_x}\right)$$

For the corresponding first term we get

$$\begin{aligned}
\frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial v_x}\right) &= \frac{d}{dt}\left(m_e v_x - eA_x^{\mathcal{B}}(\vec{r},t)\right)\\
&= m_e\frac{dv_x}{dt} - e\frac{dA_x^{\mathcal{B}}(\vec{r},t)}{dt}\\
&= m_e\frac{dv_x}{dt}\\
&\quad - e\left(\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial t} + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_x}\frac{\partial r_x}{\partial t} + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_y}\frac{\partial r_y}{\partial t} + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_z}\frac{\partial r_z}{\partial t}\right)\\
&= m_e\frac{dv_x}{dt}\\
&\quad - e\left(\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial t} + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_x}v_x + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_y}v_y + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_z}v_z\right)
\end{aligned}$$

Combining the two terms we obtain

$$m_e \frac{dv_x}{dt} - e\left(\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial t} + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_x} v_x + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_y} v_y + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_z} v_z\right)$$
$$- e\frac{\partial \phi^{\mathcal{E}}(\vec{r},t)}{\partial r_x} + e\left(v_x \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_x} + v_y \frac{\partial A_y^{\mathcal{B}}(\vec{r},t)}{\partial r_x} + v_z \frac{\partial A_z^{\mathcal{B}}(\vec{r},t)}{\partial r_x}\right) = 0$$

After some re-arrangement we can write

$$m_e \frac{dv_x}{dt} = e\frac{\partial \phi^{\mathcal{E}}(\vec{r},t)}{\partial r_x} + e\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial t}$$
$$- e\left\{v_y\left(\frac{\partial A_y^{\mathcal{B}}(\vec{r},t)}{\partial r_x} - \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_y}\right) - v_z\left(\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_z} - \frac{\partial A_z^{\mathcal{B}}(\vec{r},t)}{\partial r_x}\right)\right\}$$

which is the x-component of Eq. (2.51).

2.7 Any vector field $\vec{F}(\vec{r},t)$ can be separated in two components

$$\vec{F}(\vec{r},t) = \vec{F}_T(\vec{r},t) + \vec{F}_L(\vec{r},t)$$

where $\vec{F}_T(\vec{r},t)$ and $\vec{F}_L(\vec{r},t)$ are the transverse and longitudinal components which are defined by the following relations

$$\vec{\nabla} \cdot \vec{F}_T(\vec{r},t) = 0$$
$$\vec{\nabla} \times \vec{F}_L(\vec{r},t) = 0$$

Choosing the Coulomb gauge $\nabla \cdot \vec{A}$ for the vector potential implies therefore that the vector potential $\vec{A}$ is transverse, *i.e.* $\vec{A} = \vec{A}_T$ because the transverse component has no divergences per definition and the divergence of the longitudinal component vanishes only if $\vec{A}_L = 0$. However from the relation between the magnetic induction $\vec{\mathcal{B}}$ and the vector potential we can see that

$$\begin{aligned}
\vec{\mathcal{B}} &= \vec{\nabla} \times \vec{A}^{\,\mathcal{B}} \\
&= \vec{\nabla} \times \left(\vec{A}_T^{\,\mathcal{B}} + \vec{A}_L^{\,\mathcal{B}}\right) \\
&= \vec{\nabla} \times \vec{A}_T^{\,\mathcal{B}} + \vec{\nabla} \times \vec{A}_L^{\,\mathcal{B}}
\end{aligned}$$

However the last term is zero due to the definition of the longitudinal component and therefore we can conclude that

$$\vec{\mathcal{B}} = \vec{\nabla} \times \vec{A}_T^{\,\mathcal{B}}$$

and that the longitudinal component of the vector potential, $\vec{A}_L^{\,\mathcal{B}}$, does not contribute to the magnetic field. It can therefore be set to zero without loss of generality.

However in a time-dependent case the vector potential contributes also to the electric field

$$\begin{aligned}\vec{\mathcal{E}} &= -\vec{\nabla}\phi^{\,\mathcal{E}} - \frac{\partial \vec{A}^{\,\mathcal{B}}}{\partial t} \\ &= -\vec{\nabla}\phi^{\,\mathcal{E}} - \frac{\partial \vec{A}^{\,\mathcal{B}}_L}{\partial t} - \frac{\partial \vec{A}^{\,\mathcal{B}}_T}{\partial t}\end{aligned}$$

The contribution from the scalar potential $\phi^{\,\mathcal{E}}$ is purely longitudinal because the curl of a gradient ($\vec{\nabla} \times \vec{\nabla}\phi^{\,\mathcal{E}} = 0$) vanishes. The two components of the electric field are therefore in general given as

$$\begin{aligned}\vec{\mathcal{E}}_L &= -\vec{\nabla}\phi^{\,\mathcal{E}} - \frac{\partial \vec{A}^{\,\mathcal{B}}_L}{\partial t} \\ \vec{\mathcal{E}}_T &= -\frac{\partial \vec{A}^{\,\mathcal{B}}_T}{\partial t}\end{aligned}$$

The Coulomb gauge, $\nabla \cdot \vec{A}$ and thus $\vec{A} = \vec{A}_T$ implies that the vector potential contributes only to the transverse component of the electric field

$$\begin{aligned}\vec{\mathcal{E}}_L &= -\vec{\nabla}\phi^{\,\mathcal{E}} \\ \vec{\mathcal{E}}_T &= -\frac{\partial \vec{A}^{\,\mathcal{B}}_T}{\partial t}\end{aligned}$$

Thus, the two components of the electric field are nicely separated in the Coulomb gauge.

2.8 We proceed like in exercise 2.7. The Lagrangian is now given as

$$\mathcal{L}(\vec{r}, \vec{v}, t) = -m_e\, c^2 \sqrt{1 - \frac{\vec{v}^{\,2}}{c^2}} + e\ \phi^{\,\mathcal{E}}(\vec{r}, t) - e\ \vec{v} \cdot \vec{A}^{\,\mathcal{B}}(\vec{r}, t)$$

The second term in the (Euler)-Lagrange equations is therefore the same as in the non-relativistic case (exercise 2.7). However, the first term reads now

$$\begin{aligned}\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial v_x}\right) &= \frac{d}{dt}\left(\frac{m_e v_x}{\sqrt{1 - \frac{\vec{v}^{\,2}}{c^2}}} - eA^{\mathcal{B}}_x(\vec{r}, t)\right) \\ &= \frac{d}{dt}\frac{m_e v_x}{\sqrt{1 - \frac{\vec{v}^{\,2}}{c^2}}} - e\frac{dA^{\mathcal{B}}_x(\vec{r}, t)}{dt} \\ &= \frac{d}{dt}\frac{m_e v_x}{\sqrt{1 - \frac{\vec{v}^{\,2}}{c^2}}} \\ &\quad - e\left(\frac{\partial A^{\mathcal{B}}_x(\vec{r}, t)}{\partial t} + \frac{\partial A^{\mathcal{B}}_x(\vec{r}, t)}{\partial r_x}\frac{\partial r_x}{\partial t} + \frac{\partial A^{\mathcal{B}}_x(\vec{r}, t)}{\partial r_y}\frac{\partial r_y}{\partial t} + \frac{\partial A^{\mathcal{B}}_x(\vec{r}, t)}{\partial r_z}\frac{\partial r_z}{\partial t}\right)\end{aligned}$$

or

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial v_x}\right) = \frac{d}{dt}\frac{m_e v_x}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} - e\left(\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial t} + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_x}v_x + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_y}v_y + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_z}v_z\right)$$

Combining the two terms we obtain

$$\frac{d}{dt}\frac{m_e v_x}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} - e\left(\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial t} + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_x}v_x + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_y}v_y + \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_z}v_z\right) - e\frac{\partial \phi^{\,\mathcal{E}}(\vec{r},t)}{\partial r_x} + e\left(v_x\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_x} + v_y\frac{\partial A_y^{\mathcal{B}}(\vec{r},t)}{\partial r_x} + v_z\frac{\partial A_z^{\mathcal{B}}(\vec{r},t)}{\partial r_x}\right) = 0$$

and after some re-arrangement we can write

$$\frac{d}{dt}\frac{m_e v_x}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} = e\frac{\partial \phi^{\,\mathcal{E}}(\vec{r},t)}{\partial r_x} + e\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial t} - e\left\{v_y\left(\frac{\partial A_y^{\mathcal{B}}(\vec{r},t)}{\partial r_x} - \frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_y}\right) - v_z\left(\frac{\partial A_x^{\mathcal{B}}(\vec{r},t)}{\partial r_z} - \frac{\partial A_z^{\mathcal{B}}(\vec{r},t)}{\partial r_x}\right)\right\}$$

which is the x-component of Eq. (2.64).

2.9 Inserting the relativistic canonical momentum, Eq. (2.67), and the relativistic Lagrangian, Eq. (2.66), in the expression for the classical Hamiltonian, Eq. (2.54), gives

$$\begin{aligned}
&\mathcal{H}(\vec{r},\vec{p},t)\\
&= \left(\frac{m_e\;\vec{v}}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} - e\;\vec{A}^{\,\mathcal{B}}(\vec{r},t)\right)\cdot\vec{v} + m_e\;c^2\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}} - e\;\phi^{\,\mathcal{E}}(\vec{r},t) + e\;\vec{v}\cdot\vec{A}^{\,\mathcal{B}}(\vec{r},t)\\
&= \frac{m_e\;\vec{v}^{\,2}}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} + m_e\;c^2\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}} - e\;\phi^{\,\mathcal{E}}(\vec{r},t)\\
&= \frac{m_e\;\vec{v}^{\,2} + m_e\;c^2\left(1-\frac{\vec{v}^{\,2}}{c^2}\right)}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} - e\;\phi^{\,\mathcal{E}}(\vec{r},t)\\
&= \frac{m_e\;c^2}{\sqrt{1-\frac{\vec{v}^{\,2}}{c^2}}} - e\;\phi^{\,\mathcal{E}}(\vec{r},t)
\end{aligned}$$

However, we cannot make the transition to quantum mechanics from this Hamiltonian because it is written in terms of the velocity and not the canonical momentum. Using the expression for the canonical momentum, Eq. (2.67), we can eliminate the velocity. Before doing so we have to rearrange the expression and square it on both sides

$$\left(\mathcal{H}(\vec{r},\vec{p},t) + e\ \phi^{\mathcal{E}}(\vec{r},t)\right)^2 = \frac{m_e^2\ c^4}{1-\frac{\vec{v}^{\,2}}{c^2}}$$

The right hand side can also be written as

$$\left(\mathcal{H}(\vec{r},\vec{p},t) + e\ \phi^{\mathcal{E}}(\vec{r},t)\right)^2 = m_e^2\ c^4 + \frac{m_e^2\ c^2\ \vec{v}^{\,2}}{1-\frac{\vec{v}^{\,2}}{c^2}}$$

When we also rearrange and square the expression for the canonical momentum, Eq. (2.67), we obtain

$$\left(\vec{p} + e\ \vec{A}^{\mathcal{B}}(\vec{r},t)\right)^2 = \frac{m_e^2\ \vec{v}^{\,2}}{1-\frac{\vec{v}^{\,2}}{c^2}}$$

and can therefore identify the second term of the right hand side of the previous equation as

$$\frac{m_e^2\ c^2\ \vec{v}^{\,2}}{1-\frac{\vec{v}^{\,2}}{c^2}} = c^2\left(\vec{p} + e\ \vec{A}^{\mathcal{B}}(\vec{r},t)\right)^2$$

The Hamiltonian becomes therefore

$$\mathcal{H}(\vec{r},\vec{p},t) = \sqrt{m_e^2\ c^4 + c^2\left(\vec{p} + e\ \vec{A}^{\mathcal{B}}(\vec{r},t)\right)^2} - e\ \phi^{\mathcal{E}}(\vec{r},t)$$

2.10 In order to show that

$$\boldsymbol{\alpha}_\mu^2 = \boldsymbol{\beta}^2 = \begin{pmatrix} \boldsymbol{I} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{I} \end{pmatrix} \qquad \text{for } \mu = x,y,z$$

$$\boldsymbol{\alpha}_\mu\boldsymbol{\alpha}_\nu + \boldsymbol{\alpha}_\nu\boldsymbol{\alpha}_\mu = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \qquad \text{for } \mu \neq \nu$$

$$\boldsymbol{\alpha}_\mu\boldsymbol{\beta} + \boldsymbol{\beta}\boldsymbol{\alpha}_\mu = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \qquad \text{for } \mu = x,y,z$$

we make use of the commutator and anti-commutator relations of the Pauli spin matrices

$$[\boldsymbol{\sigma}_i, \boldsymbol{\sigma}_j] = 2\ \imath\ \epsilon_{ijk}\ \boldsymbol{\sigma}_k \quad \text{or} \quad \boldsymbol{\sigma}_i\boldsymbol{\sigma}_j = \imath\ \epsilon_{ijk}\ \boldsymbol{\sigma}_k$$

and

$$[\boldsymbol{\sigma}_i, \boldsymbol{\sigma}_j]_+ = 2\ \delta_{ij}\ \boldsymbol{I} \quad \text{or} \quad \boldsymbol{\sigma}_i\boldsymbol{\sigma}_i = \boldsymbol{I}$$

where ϵ_{ijk} is the Levi-Civita symbol [**?**].

We obtain then for

$$\boldsymbol{\alpha}_\mu^2 = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_\mu \\ \boldsymbol{\sigma}_\mu & \mathbf{0} \end{pmatrix}\begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_\mu \\ \boldsymbol{\sigma}_\mu & \mathbf{0} \end{pmatrix} = \begin{pmatrix} \boldsymbol{\sigma}_\mu^2 & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\sigma}_\mu^2 \end{pmatrix} = \begin{pmatrix} \boldsymbol{I} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{I} \end{pmatrix}$$

$$\boldsymbol{\beta}^2 = \begin{pmatrix} \boldsymbol{I} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{I} \end{pmatrix}\begin{pmatrix} \boldsymbol{I} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{I} \end{pmatrix} = \begin{pmatrix} \boldsymbol{I} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{I} \end{pmatrix}$$

$$\boldsymbol{\alpha}_\mu\boldsymbol{\alpha}_\nu + \boldsymbol{\alpha}_\nu\boldsymbol{\alpha}_\mu = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_\mu \\ \boldsymbol{\sigma}_\mu & \mathbf{0} \end{pmatrix}\begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_\nu \\ \boldsymbol{\sigma}_\nu & \mathbf{0} \end{pmatrix} + \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_\nu \\ \boldsymbol{\sigma}_\nu & \mathbf{0} \end{pmatrix}\begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_\mu \\ \boldsymbol{\sigma}_\mu & \mathbf{0} \end{pmatrix}$$
$$= \begin{pmatrix} \boldsymbol{\sigma}_\mu\boldsymbol{\sigma}_\nu & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\sigma}_\mu\boldsymbol{\sigma}_\nu \end{pmatrix} + \begin{pmatrix} \boldsymbol{\sigma}_\nu\boldsymbol{\sigma}_\mu & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\sigma}_\nu\boldsymbol{\sigma}_\mu \end{pmatrix}$$
$$= \begin{pmatrix} [\boldsymbol{\sigma}_\mu, \boldsymbol{\sigma}_\nu]_+ & \mathbf{0} \\ \mathbf{0} & [\boldsymbol{\sigma}_\mu, \boldsymbol{\sigma}_\nu]_+ \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}$$

$$\boldsymbol{\alpha}_\mu\boldsymbol{\beta} + \boldsymbol{\beta}\boldsymbol{\alpha}_\mu = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_\mu \\ \boldsymbol{\sigma}_\mu & \mathbf{0} \end{pmatrix}\begin{pmatrix} \boldsymbol{I} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{I} \end{pmatrix} + \begin{pmatrix} \boldsymbol{I} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{I} \end{pmatrix}\begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_\mu \\ \boldsymbol{\sigma}_\mu & \mathbf{0} \end{pmatrix}$$
$$= \begin{pmatrix} \mathbf{0} & -\boldsymbol{\sigma}_\mu \\ \boldsymbol{\sigma}_\mu & \mathbf{0} \end{pmatrix} + \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_\mu \\ -\boldsymbol{\sigma}_\mu & \mathbf{0} \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}$$

2.11

$$\left(\sum_{\alpha=x,y,z} \boldsymbol{\sigma}_\alpha \hat{C}_\alpha\right)\left(\sum_{\beta=x,y,z} \boldsymbol{\sigma}_\beta \hat{D}_\beta\right) = \boldsymbol{\sigma}_x\hat{C}_x\boldsymbol{\sigma}_x\hat{D}_x + \boldsymbol{\sigma}_x\hat{C}_x\boldsymbol{\sigma}_y\hat{D}_y + \boldsymbol{\sigma}_x\hat{C}_x\boldsymbol{\sigma}_z\hat{D}_z$$
$$+ \boldsymbol{\sigma}_y\hat{C}_y\boldsymbol{\sigma}_x\hat{D}_x + \boldsymbol{\sigma}_y\hat{C}_y\boldsymbol{\sigma}_y\hat{D}_y + \boldsymbol{\sigma}_y\hat{C}_y\boldsymbol{\sigma}_z\hat{D}_z$$
$$+ \boldsymbol{\sigma}_z\hat{C}_z\boldsymbol{\sigma}_x\hat{D}_x + \boldsymbol{\sigma}_z\hat{C}_z\boldsymbol{\sigma}_y\hat{D}_y + \boldsymbol{\sigma}_z\hat{C}_z\boldsymbol{\sigma}_z\hat{D}_z$$

Using that $[\boldsymbol{\sigma}_\alpha, \hat{C}_\beta] = 0$ and $[\boldsymbol{\sigma}_\alpha, \hat{D}_\beta] = 0$ we obtain

$$= \boldsymbol{\sigma}_x^2\hat{C}_x\hat{D}_x + \boldsymbol{\sigma}_x\boldsymbol{\sigma}_y\hat{C}_x\hat{D}_y + \boldsymbol{\sigma}_x\boldsymbol{\sigma}_z\hat{C}_x\hat{D}_z$$
$$+ \boldsymbol{\sigma}_y\boldsymbol{\sigma}_x\hat{C}_y\hat{D}_x + \boldsymbol{\sigma}_y^2\hat{C}_y\hat{D}_y + \boldsymbol{\sigma}_y\boldsymbol{\sigma}_z\hat{C}_y\hat{D}_z + \boldsymbol{\sigma}_z\boldsymbol{\sigma}_x\hat{C}_z\hat{D}_x + \boldsymbol{\sigma}_z\boldsymbol{\sigma}_y\hat{C}_z\hat{D}_y + \boldsymbol{\sigma}_z^2\hat{C}_z\hat{D}_z$$

Using that $\boldsymbol{\sigma}_i\boldsymbol{\sigma}_j = \imath\, \epsilon_{ijk}\, \boldsymbol{\sigma}_k$ and $\boldsymbol{\sigma}_i\boldsymbol{\sigma}_i = \boldsymbol{I}$ we can write

$$= \boldsymbol{I}\ \hat{C}_x\hat{D}_x + \boldsymbol{I}\ \hat{C}_y\hat{D}_y + \boldsymbol{I}\ \hat{C}_z\hat{D}_z$$
$$+ \imath\boldsymbol{\sigma}_x\left(\hat{C}_y\hat{D}_z - \hat{C}_z\hat{D}_y\right) + \imath\boldsymbol{\sigma}_y\left(\hat{C}_z\hat{D}_x - \hat{C}_x\hat{D}_z\right) + \imath\boldsymbol{\sigma}_z\left(\hat{C}_x\hat{D}_y - \hat{C}_y\hat{D}_x\right)$$
$$= \left(\hat{\vec{C}} \cdot \hat{\vec{D}}\right)\boldsymbol{I} + \imath \sum_{\alpha=x,y,z} \boldsymbol{\sigma}_\alpha \left(\hat{\vec{C}} \times \hat{\vec{D}}\right)_\alpha$$

2.12 We will show that

$$\hat{\vec{\nabla}} \times \left(\hat{\vec{C}}\psi\right) = -\hat{\vec{C}} \times \hat{\vec{\nabla}}\psi + \left(\hat{\vec{\nabla}} \times \hat{\vec{C}}\right)\psi$$

for the x-component:

$$\left[\hat{\vec{\nabla}} \times \left(\hat{\vec{C}}\psi\right)\right]_x = \frac{\partial}{\partial y}\left(\hat{C}_z\psi\right) - \frac{\partial}{\partial z}\left(\hat{C}_y\psi\right)$$
$$= \left(\frac{\partial}{\partial y}\hat{C}_z\right)\psi + \hat{C}_z\frac{\partial}{\partial y}\psi - \left(\frac{\partial}{\partial z}\hat{C}_y\right)\psi - \hat{C}_y\frac{\partial}{\partial z}\psi$$
$$= \left[\hat{\vec{\nabla}} \times \hat{\vec{C}}\right]_x\psi - \left[\hat{\vec{C}} \times \hat{\vec{\nabla}}\psi\right]_x$$

2.13 Using equation Eq. (2.90) we can rewrite

$$\left(\sum_{\alpha=x,y,z} \boldsymbol{\sigma}_\alpha \left(\hat{p}_\alpha + e\,\hat{A}^{\mathcal{B}}_\alpha(\vec{r})\right)\right) \left(\sum_{\alpha=x,y,z} \boldsymbol{\sigma}_\alpha \left(\hat{p}_\alpha + e\,\hat{A}^{\mathcal{B}}_\alpha(\vec{r})\right)\right) |\bar{\psi}_L\rangle$$

as

$$\left(\left(\hat{\vec{p}} + e\,\hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right)^2 + \imath \sum_{\alpha=x,y,z} \boldsymbol{\sigma}_\alpha \left[\left(\hat{\vec{p}} + e\,\hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right) \times \left(\hat{\vec{p}} + e\,\hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right)\right]_\alpha\right) |\bar{\psi}_L\rangle$$

On expansion of the cross product we obtain

$$\left(\left(\hat{\vec{p}} + e\,\hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right)^2 + \imath \sum_{\alpha=x,y,z} \boldsymbol{\sigma}_\alpha \left[e\,\hat{\vec{p}} \times \hat{\vec{A}}^{\mathcal{B}}(\vec{r}) + e\,\hat{\vec{A}}^{\mathcal{B}}(\vec{r}) \times \hat{\vec{p}}\right]_\alpha\right) |\bar{\psi}_L\rangle$$

because the cross product of a vector with itself is zero. Since $\hat{\vec{p}} = -\imath\hbar\hat{\vec{\nabla}}$, we can make use of Eq. (2.91) and obtain

$$\left(\left(\hat{\vec{p}} + e\,\hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right)^2 + \hbar e \sum_{\alpha=x,y,z} \boldsymbol{\sigma}_\alpha \left[-\hat{\vec{A}}^{\mathcal{B}}(\vec{r}) \times \hat{\vec{\nabla}} + \left(\hat{\vec{\nabla}} \times \hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right) + \hat{\vec{A}}^{\mathcal{B}}(\vec{r}) \times \hat{\vec{\nabla}}\right]_\alpha\right) |\bar{\psi}_L\rangle$$

or

$$\left(\left(\hat{\vec{p}} + e\,\hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right)^2 + \hbar e \sum_{\alpha=x,y,z} \boldsymbol{\sigma}_\alpha \left(\hat{\vec{\nabla}} \times \hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right)_\alpha\right) |\bar{\psi}_L\rangle$$

2.14 In order to proof that we let $\left(\hat{H} - \imath\hbar\frac{\partial}{\partial t}\right)$ act on $e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}|\psi(t)\rangle$. This should then give $e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\left(\hat{H}' - \imath\hbar\frac{\partial}{\partial t}\right)|\psi(t)\rangle$. Let us therefore start with $\hat{H}e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}|\psi(t)\rangle$

$$\hat{H}e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}|\psi(t)\rangle = \left\{\frac{1}{2m_e}\left(\hat{\vec{p}} + e\hat{\vec{A}}^{\,\mathcal{B}}(\vec{r},t)\right)^2 - e\;\hat{\phi}^{\mathcal{E}}(\vec{r},t)\right\} e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}|\psi(t)\rangle$$

Inserting the expression for the canonical momentum operator, expanding the outermost parenthesis and expanding the square we can write

$$\begin{aligned} &= \frac{1}{2m_e}\left(-\imath\hbar\hat{\vec{\nabla}} + e\hat{\vec{A}}^{\,\mathcal{B}}(\vec{r},t)\right)\left(-\imath\hbar\hat{\vec{\nabla}} + e\hat{\vec{A}}^{\,\mathcal{B}}(\vec{r},t)\right) e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}|\psi(t)\rangle \\ &\quad - e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\; e\;\hat{\phi}^{\mathcal{E}}(\vec{r},t)|\psi(t)\rangle \end{aligned}$$

Letting the right parenthesis act on the transformed wavefunction gives

$$\begin{aligned} &= \frac{1}{2m_e}\left(-\imath\hbar\hat{\vec{\nabla}} + e\hat{\vec{A}}^{\,\mathcal{B}}(\vec{r},t)\right) e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\left(e\hat{\vec{\nabla}}\chi(\vec{r},t) - \imath\hbar\hat{\vec{\nabla}} + e\hat{\vec{A}}^{\,\mathcal{B}}(\vec{r},t)\right)|\psi(t)\rangle \\ &\quad - e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\; e\;\hat{\phi}^{\mathcal{E}}(\vec{r},t)|\psi(t)\rangle \end{aligned}$$

Expansion of the left parenthesis gives

$$\begin{aligned}
&= -\frac{1}{2m_e}\,\imath\hbar\hat{\vec{\nabla}}e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\left(-\imath\hbar\hat{\vec{\nabla}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t) + \hat{\vec{\nabla}}\chi(\vec{r},t)\right)\right)|\psi(t)\rangle \\
&\quad + e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\frac{1}{2m_e}\,e\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t)\left(-\imath\hbar\hat{\vec{\nabla}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t) + \hat{\vec{\nabla}}\chi(\vec{r},t)\right)\right)|\psi(t)\rangle \\
&\quad - e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\,e\;\hat{\phi}^{\mathcal{E}}(\vec{r},t)|\psi(t)\rangle
\end{aligned}$$

Application of the gradient operator in the first line gives

$$\begin{aligned}
&= e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\frac{1}{2m_e}\,e\hat{\vec{\nabla}}\chi(\vec{r},t)\left(-\imath\hbar\hat{\vec{\nabla}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t) + \hat{\vec{\nabla}}\chi(\vec{r},t)\right)\right)|\psi(t)\rangle \\
&\quad - e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\frac{1}{2m_e}\,\imath\hbar\hat{\vec{\nabla}}\left(-\imath\hbar\hat{\vec{\nabla}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t) + \hat{\vec{\nabla}}\chi(\vec{r},t)\right)\right)|\psi(t)\rangle \\
&\quad + e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\frac{1}{2m_e}\,e\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t)\left(-\imath\hbar\hat{\vec{\nabla}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t) + \hat{\vec{\nabla}}\chi(\vec{r},t)\right)\right)|\psi(t)\rangle \\
&\quad - e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\,e\;\hat{\phi}^{\mathcal{E}}(\vec{r},t)|\psi(t)\rangle
\end{aligned}$$

Collecting terms we obtain

$$\begin{aligned}
&= e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\frac{1}{2m_e}\left(-\imath\hbar\hat{\vec{\nabla}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t) + \hat{\vec{\nabla}}\chi(\vec{r},t)\right)\right) \\
&\quad \cdot\left(-\imath\hbar\hat{\vec{\nabla}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t) + \hat{\vec{\nabla}}\chi(\vec{r},t)\right)\right)|\psi(t)\rangle \\
&\quad - e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\,e\;\hat{\phi}^{\mathcal{E}}(\vec{r},t)|\psi(t)\rangle
\end{aligned}$$

or finally

$$\hat{H}e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}|\psi(t)\rangle = e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\left\{\frac{1}{2m_e}\left(\hat{\vec{p}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t) + \hat{\vec{\nabla}}\chi(\vec{r},t)\right)\right)^2 - e\;\hat{\phi}^{\mathcal{E}}(\vec{r},t)\right\}|\psi(t)\rangle$$

Now we have to apply $-\imath\hbar\frac{\partial}{\partial t}$ to $e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}|\psi(t)\rangle$

$$-\imath\hbar\frac{\partial}{\partial t}e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}|\psi(t)\rangle = e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}e\frac{\partial\chi(\vec{r},t)}{\partial t}|\psi(t)\rangle - \imath\hbar e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\frac{\partial}{\partial t}|\psi(t)\rangle$$

Combined with the previous results we obtain

$$\begin{aligned}
\left(\hat{H} - \imath\hbar\frac{\partial}{\partial t}\right)e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}|\psi(t)\rangle &= e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\left\{\frac{1}{2m_e}\left(\hat{\vec{p}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r},t) + \hat{\vec{\nabla}}\chi(\vec{r},t)\right)\right)^2\right. \\
&\qquad \left. - e\left(\hat{\phi}^{\mathcal{E}}(\vec{r},t) - \frac{\partial\chi(\vec{r},t)}{\partial t}\right) - \imath\hbar\frac{\partial}{\partial t}\right\}|\psi(t)\rangle \\
&= e^{\imath\frac{e}{\hbar}\chi(\vec{r},t)}\left(\hat{H}' - \imath\hbar\frac{\partial}{\partial t}\right)|\psi(t)\rangle
\end{aligned}$$

2.15 We have to proof two things. First that

$$\begin{aligned}\langle\psi'\,|\,\hat{\vec{\pi}}'\,|\,\psi'\rangle &= \langle e^{-\imath\frac{e}{\hbar}\chi(\vec{r})}\psi\,|\,e^{-\imath\frac{e}{\hbar}\chi(\vec{r})}\,\hat{\vec{\pi}}\,e^{\imath\frac{e}{\hbar}\chi(\vec{r})}\,|\,e^{-\imath\frac{e}{\hbar}\chi(\vec{r})}\psi\rangle \\ &= \langle\psi\,|\,e^{\imath\frac{e}{\hbar}\chi(\vec{r})}e^{-\imath\frac{e}{\hbar}\chi(\vec{r})}\,\hat{\vec{\pi}}\,e^{\imath\frac{e}{\hbar}\chi(\vec{r})}e^{-\imath\frac{e}{\hbar}\chi(\vec{r})}\,|\,\psi\rangle = \langle\psi\,|\,\hat{\vec{\pi}}\,|\,\psi\rangle\end{aligned}$$

which is hereby already shown, and secondly that

$$\hat{\vec{\pi}}' = e^{-\imath\frac{e}{\hbar}\chi(\vec{r})}\,\hat{\vec{\pi}}\,e^{\imath\frac{e}{\hbar}\chi(\vec{r})} = \hat{\vec{p}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r}) + \hat{\vec{\nabla}}\chi(\vec{r})\right)$$

The proof is completely analog to the solution to exercise 2.14.

$$\hat{\vec{\pi}}\,e^{\imath\frac{e}{\hbar}\chi(\vec{r})}|\psi\rangle = \left(\hat{\vec{p}} + e\hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right)e^{\imath\frac{e}{\hbar}\chi(\vec{r})}|\psi\rangle$$

Inserting the expression for the canonical momentum operator we can write

$$\begin{aligned}\hat{\vec{\pi}}\,e^{\imath\frac{e}{\hbar}\chi(\vec{r})}|\psi\rangle &= \left(-\imath\hbar\hat{\vec{\nabla}} + e\hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right)e^{\imath\frac{e}{\hbar}\chi(\vec{r})}|\psi\rangle \\ &= e^{\imath\frac{e}{\hbar}\chi(\vec{r})}\left(e\hat{\vec{\nabla}}\chi(\vec{r}) - \imath\hbar\hat{\vec{\nabla}} + e\hat{\vec{A}}^{\mathcal{B}}(\vec{r})\right)|\psi\rangle \\ &= e^{\imath\frac{e}{\hbar}\chi(\vec{r})}\left(\hat{\vec{p}} + e\left(\hat{\vec{A}}^{\mathcal{B}}(\vec{r}) + \hat{\vec{\nabla}}\chi(\vec{r})\right)\right)|\psi\rangle\end{aligned}$$

Solutions to Chapter 3

3.1 Projecting

$$|\,\Psi_0^{(m)}(\vec{\mathcal{F}})\rangle = \sum_{l\neq 0} |\Psi_l^{(0)}\rangle\; C_{l0}^{(m)}(\vec{\mathcal{F}})$$

on the unperturbed bra $\langle\Psi_n^{(0)}|$, now for a change, we obtain

$$\langle\Psi_n^{(0)}\mid\Psi_0^{(m)}(\vec{\mathcal{F}})\rangle = \sum_{l\neq 0}\langle\Psi_n^{(0)}\mid\Psi_l^{(0)}\rangle\; C_{l0}^{(m)}(\vec{\mathcal{F}})$$

But the unperturbed wavefunctions $|\Psi_l^{(0)}\rangle$ are orthonormalized

$$\langle\Psi_n^{(0)}\mid\Psi_l^{(0)}\rangle = \delta_{nl}$$

and thus

$$\langle\Psi_n^{(0)}\mid\Psi_0^{(m)}(\vec{\mathcal{F}})\rangle = \sum_{l\neq 0}\delta_{nl}\; C_{l0}^{(m)}(\vec{\mathcal{F}}) = C_{n0}^{(m)}(\vec{\mathcal{F}})$$

3.2 Projecting the first-order equation

$$\hat{H}^{(0)}|\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(1)}|\Psi_0^{(0)}\rangle = E_0^{(0)}|\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})|\Psi_0^{(0)}\rangle$$

again but now on the unperturbed bra $\langle\Psi_n^{(0)}|$ we obtain

$$\begin{aligned}\langle\Psi_n^{(0)}\,|\,\hat{H}^{(0)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle &+ \langle\Psi_n^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(0)}\rangle \\ &= E_0^{(0)}\langle\Psi_n^{(0)}\mid\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})\langle\Psi_n^{(0)}\mid\Psi_0^{(0)}\rangle\end{aligned}$$

Using again that the unperturbed wavefunctions $|\Psi_n^{(0)}\rangle$ are orthogonal and eigenfunctions of $\hat{H}^{(0)}$ we can write

$$E_n^{(0)}\langle\Psi_n^{(0)}\mid\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_n^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(0)}\rangle = E_0^{(0)}\langle\Psi_n^{(0)}\mid\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle$$

or

$$\langle\Psi_n^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(0)}\rangle = \left(E_0^{(0)} - E_n^{(0)}\right)\langle\Psi_n^{(0)}\mid\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle$$

But $\langle\Psi_n^{(0)}\mid\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle = C_{n0}^{(1)}(\vec{\mathcal{F}})$ according to Exercise 3.1 and for $E_0^{(0)} \neq E_n^{(0)}$ we obtain thus

$$C_{n0}^{(1)}(\vec{\mathcal{F}}) = \frac{\langle\Psi_n^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}$$

3.3 First, we determine the second-order coefficients. The second-order equation reads

$$\hat{H}^{(0)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(1)}|\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(2)}|\Psi_0^{(0)}\rangle = E_0^{(0)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})|\Psi_0^{(1)}\rangle + E_0^{(2)}(\vec{\mathcal{F}})|\Psi_0^{(0)}\rangle$$

Projecting onto an unperturbed state $\langle\Psi_n^{(0)}|$ gives

$$\langle\Psi_n^{(0)}|\hat{H}^{(0)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \langle\Psi_n^{(0)}|\hat{H}^{(1)}|\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_n^{(0)}|\hat{H}^{(2)}|\Psi_0^{(0)}\rangle = E_0^{(0)}\langle\Psi_n^{(0)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})\langle\Psi_n^{(0)}|\Psi_0^{(1)}\rangle + E_0^{(2)}(\vec{\mathcal{F}})\langle\Psi_n^{(0)}|\Psi_0^{(0)}\rangle$$

which reduces to

$$E_n^{(0)}\langle\Psi_n^{(0)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \langle\Psi_n^{(0)}|\hat{H}^{(1)}|\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_n^{(0)}|\hat{H}^{(2)}|\Psi_0^{(0)}\rangle = E_0^{(0)}\langle\Psi_n^{(0)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})\langle\Psi_n^{(0)}|\Psi_0^{(1)(\vec{\mathcal{F}})}\rangle$$

by applying the Hermiticity of the unperturbed Hamiltonian and the orthonormality of the unperturbed eigenfunctions. Inserting the expansions for the first- and second-order corrections to the wavefunction, Eq. (3.23), gives

$$E_n^{(0)}\sum_{m\neq 0}\langle\Psi_n^{(0)}|\Psi_m^{(0)}\rangle C_{m0}^{(2)}(\vec{\mathcal{F}}) + \sum_{k\neq 0}\langle\Psi_n^{(0)}|\hat{H}^{(1)}|\Psi_k^{(0)}\rangle C_{k0}^{(1)}(\vec{\mathcal{F}}) + \langle\Psi_n^{(0)}|\hat{H}^{(2)}|\Psi_0^{(0)}\rangle = E_0^{(0)}\sum_{m\neq 0}\langle\Psi_n^{(0)}|\Psi_m^{(0)}\rangle C_{m0}^{(2)}(\vec{\mathcal{F}}) + E_0^{(1)}(\vec{\mathcal{F}})\sum_{k\neq 0}\langle\Psi_n^{(0)}|\Psi_k^{(0)}\rangle C_{k0}^{(1)}(\vec{\mathcal{F}})$$

or

$$E_n^{(0)}\sum_{m\neq 0}\delta_{nm}C_{m0}^{(2)}(\vec{\mathcal{F}}) + \sum_{k\neq 0}\langle\Psi_n^{(0)}|\hat{H}^{(1)}|\Psi_k^{(0)}\rangle C_{k0}^{(1)}(\vec{\mathcal{F}}) + \langle\Psi_n^{(0)}|\hat{H}^{(2)}|\Psi_0^{(0)}\rangle = E_0^{(0)}\sum_{m\neq 0}\delta_{nm}C_{m0}^{(2)}(\vec{\mathcal{F}}) + E_0^{(1)}(\vec{\mathcal{F}})\sum_{k\neq 0}\delta_{nk}C_{k0}^{(1)}(\vec{\mathcal{F}})$$

and finally

$$E_n^{(0)}C_{n0}^{(2)}(\vec{\mathcal{F}}) + \sum_{k\neq 0}\langle\Psi_n^{(0)}|\hat{H}^{(1)}|\Psi_k^{(0)}\rangle C_{k0}^{(1)}(\vec{\mathcal{F}}) + \langle\Psi_n^{(0)}|\hat{H}^{(2)}|\Psi_0^{(0)}\rangle = E_0^{(0)}C_{n0}^{(2)}(\vec{\mathcal{F}}) + E_0^{(1)}(\vec{\mathcal{F}})C_{n0}^{(1)}(\vec{\mathcal{F}})$$

The second-order coefficients therefore become

$$C_{n0}^{(2)}(\vec{\mathcal{F}}) = \frac{\langle\Psi_n^{(0)}|\hat{H}^{(2)}|\Psi_0^{(0)}\rangle - E_0^{(1)}(\vec{\mathcal{F}})C_{n0}^{(1)}(\vec{\mathcal{F}})}{(E_0^{(0)} - E_n^{(0)})} + \sum_{k\neq 0}\frac{\langle\Psi_n^{(0)}|\hat{H}^{(1)}|\Psi_k^{(0)}\rangle C_{k0}^{(1)}(\vec{\mathcal{F}})}{(E_0^{(0)} - E_n^{(0)})}$$

As we show in Exercise 3.4, the first-order correction to the energy can be written as an expectation value of the first-order perturbation Hamiltonian over the unperturbed wavefunction

$$E_0^{(1)}(\vec{\mathcal{F}}) = \langle\Psi_0^{(0)}|\hat{H}^{(1)}|\Psi_0^{(0)}\rangle$$

Inserting the first-order correction to the energy and the first-order coefficients yields

$$C_{n0}^{(2)}(\vec{\mathcal{F}}) = \frac{\langle \Psi_n^{(0)} | \hat{H}^{(2)} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} - \frac{\langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle}{(E_0^{(0)} - E_n^{(0)})^2}$$
$$+ \sum_{k \neq 0} \frac{\langle \Psi_n^{(0)} | \hat{H}^{(1)} | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_k^{(0)})}$$

The second-order correction to the wavefunction therefore becomes thus

$$|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle = \sum_{n \neq 0} |\Psi_n^{(0)}\rangle \left[\frac{\langle \Psi_n^{(0)} | \hat{H}^{(2)} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} - \frac{\langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle}{(E_0^{(0)} - E_n^{(0)})^2} \right.$$
$$\left. + \sum_{k \neq 0} \frac{\langle \Psi_n^{(0)} | \hat{H}^{(1)} | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle}{(E_0^{(0)} - E_n^{(0)})(E_0^{(0)} - E_k^{(0)})} \right]$$

3.4 Projecting the first-order equation

$$\hat{H}^{(0)} |\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(1)} |\Psi_0^{(0)}\rangle = E_0^{(0)} |\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}}) |\Psi_0^{(0)}\rangle$$

on the unperturbed bra $\langle \Psi_0^{(0)}|$ we obtain

$$\langle \Psi_0^{(0)} \,|\, \hat{H}^{(0)} \,|\, \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \langle \Psi_0^{(0)} \,|\, \hat{H}^{(1)} \,|\, \Psi_0^{(0)}\rangle$$
$$= E_0^{(0)} \langle \Psi_0^{(0)} \mid \Psi_0^{(1)}(\vec{\mathcal{F}}\rangle + E_0^{(1)}(\vec{\mathcal{F}}) \langle \Psi_0^{(0)} \mid \Psi_0^{(0)}\rangle$$

Using that the unperturbed wavefunction $|\Psi_0^{(0)}\rangle$ is normalized

$$\langle \Psi_0^{(0)} \mid \Psi_0^{(0)}\rangle = 1$$

and that it is an eigenfunction of $\hat{H}^{(0)}$, *i.e.*

$$\langle \Psi_0^{(0)}| \; \hat{H}^{(0)} = \langle \Psi_0^{(0)}| \; E_0^{(0)}$$

we can write

$$E_0^{(0)} \langle \Psi_0^{(0)} \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \langle \Psi_0^{(0)} \,|\, \hat{H}^{(1)} \,|\, \Psi_0^{(0)}\rangle = E_0^{(0)} \langle \Psi_0^{(0)} \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})$$

and thus

$$E_0^{(1)}(\vec{\mathcal{F}}) = \langle \Psi_0^{(0)} \,|\, \hat{H}^{(1)} \,|\, \Psi_0^{(0)}\rangle$$

Note that for the first-order energy correction it is not necessary to use the consequence of the intermediate normalization, *i.e.*

$$\langle \Psi_0^{(0)} \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle = 0$$

Projecting similarly the second-order equation

$$\hat{H}^{(0)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(1)}|\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(2)}|\Psi_0^{(0)}\rangle$$
$$= E_0^{(0)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})|\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(2)}(\vec{\mathcal{F}})|\Psi_0^{(0)}\rangle$$

on the unperturbed bra $\langle\Psi_0^{(0)}|$ we obtain

$$\langle\Psi_0^{(0)}\,|\,\hat{H}^{(0)}\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(0)}\rangle$$
$$= E_0^{(0)}\langle\Psi_0^{(0)} \mid \Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)} \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(2)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)} \mid \Psi_0^{(0)}\rangle$$

Using again that the unperturbed wavefunction $|\Psi_0^{(0)}\rangle$ is normalized and an eigenfunction of $\hat{H}^{(0)}$ we can write

$$E_0^{(0)}\langle\Psi_0^{(0)} \mid \Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}}\rangle + \langle\Psi_0^{(0)}\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(0)}\rangle$$
$$= E_0^{(0)}\langle\Psi_0^{(0)} \mid \Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)} \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(2)}(\vec{\mathcal{F}})$$

The two terms $E_0^{(0)}\langle\Psi_0^{(0)} \mid \Psi_0^{(2)}(\vec{\mathcal{F}})\rangle$ cancel again, but for the term $E_0^{(1)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)} \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle$ we have to use now that

$$\langle\Psi_0^{(0)} \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle = 0$$

due to the intermediate normalization. This leads then to

$$E_0^{(2)}(\vec{\mathcal{F}}) = \langle\Psi_0^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(0)}\rangle$$

For a Hamiltonian quadratic in the perturbation, the mth-order equation reads

$$\hat{H}^{(0)}|\Psi_0^{(m)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(1)}|\Psi_0^{(m-1)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(2)}|\Psi_0^{(m-2)}(\vec{\mathcal{F}})\rangle$$
$$= E_0^{(0)}|\Psi_0^{(m)}(\vec{\mathcal{F}})\rangle + \sum_{i=1}^{m-1} E_0^{(i)}(\vec{\mathcal{F}})|\Psi_0^{(m-i)}(\vec{\mathcal{F}})\rangle + E_0^{(m)}(\vec{\mathcal{F}})|\Psi_0^{(0)}\rangle$$

Projecting onto the unperturbed ground state gives

$$\langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_0^{(m)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}|\hat{H}^{(1)}|\Psi_0^{(m-1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}|\hat{H}^{(2)}|\Psi_0^{(m-2)}(\vec{\mathcal{F}})\rangle$$
$$= E_0^{(0)}\langle\Psi_0^{(0)}|\Psi_0^{(m)}(\vec{\mathcal{F}})\rangle + \sum_{i=1}^{m-1} E_0^{(i)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)}|\Psi_0^{(m-i)}(\vec{\mathcal{F}})\rangle + E_0^{(m)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle$$

or

$$E_0^{(0)}\langle\Psi_0^{(0)}|\Psi_0^{(m)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}|\hat{H}^{(1)}|\Psi_0^{(m-1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}|\hat{H}^{(2)}|\Psi_0^{(m-2)}(\vec{\mathcal{F}})\rangle$$
$$= E_0^{(0)}\langle\Psi_0^{(0)}|\Psi_0^{(m)}(\vec{\mathcal{F}})\rangle + \sum_{i=1}^{m-1} E_0^{(i)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)}|\Psi_0^{(m-i)}(\vec{\mathcal{F}})\rangle + E_0^{(m)}(\vec{\mathcal{F}})$$

Again, we apply the intermediate normalization condition and obtain for the mth-order correction to the energy

$$E_0^{(m)}(\vec{\mathcal{F}}) = \langle\Psi_0^{(0)}|\hat{H}^{(1)}|\Psi_0^{(m-1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}|\hat{H}^{(2)}|\Psi_0^{(m-2)}(\vec{\mathcal{F}})\rangle$$

3.5 In order to derive an expression for the third-order energy correction we have to start from the third-order equation

$$\hat{H}^{(0)}|\Psi_0^{(3)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(1)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \hat{H}^{(2)}|\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle$$
$$= E_0^{(0)}|\Psi_0^{(3)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + E_0^{(2)}|\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(3)}(\vec{\mathcal{F}})|\Psi_0^{(0)}\rangle$$

which we again project on the unperturbed bra $\langle\Psi_0^{(0)}|$

$$\langle\Psi_0^{(0)}\,|\,\hat{H}^{(0)}\,|\,\Psi_0^{(3)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle$$
$$= E_0^{(0)}\langle\Psi_0^{(0)} \mid \Psi_0^{(3)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)} \mid \Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + E_0^{(2)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)} \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle$$
$$+ E_0^{(3)}(\vec{\mathcal{F}})\langle\Psi_0^{(0)} \mid \Psi_0^{(0)}\rangle$$

Using again that the unperturbed wavefunction $|\Psi_0^{(0)}\rangle$ is normalized and an eigenfunction of $\hat{H}^{(0)}$ and that

$$\langle\Psi_0^{(0)} \mid \Psi_0^{(m)}(\vec{\mathcal{F}})\rangle = 0$$

due to the intermediate normalization, we obtain for the third-order energy correction

$$E_0^{(3)}(\vec{\mathcal{F}}) = \langle\Psi_0^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(0)}\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle$$

However in order to evaluate the first time one needs to know the second-order correction to the wavefunction, $|\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle$. On the other hand, if one recalls that

$$\langle\Psi_0^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle = \langle\Psi_0^{(2)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(0)}\rangle^*$$

we can obtain this term by projecting the first order equation on $\langle\Psi_0^{(2)}(\vec{\mathcal{F}})|$

$$\langle\Psi_0^{(2)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(0)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(2)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(0)}\rangle$$
$$= E_0^{(0)}\langle\Psi_0^{(2)}(\vec{\mathcal{F}}) \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})\langle\Psi_0^{(2)}(\vec{\mathcal{F}}) \mid \Psi_0^{(0)}\rangle$$

Using again the intermediate normalization and rearranging we obtain

$$\langle\Psi_0^{(2)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(0)}\rangle = \langle\Psi_0^{(2)}(\vec{\mathcal{F}})\,|\,E_0^{(0)} - \hat{H}^{(0)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle$$

If we recall now that

$$\langle\Psi_0^{(2)}(\vec{\mathcal{F}})\,|\,E_0^{(0)} - \hat{H}^{(0)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle = \langle\Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,E_0^{(0)} - \hat{H}^{(0)}\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle^*$$

we can obtain this term by projecting the second order equation now on $\langle\Psi_0^{(1)}(\vec{\mathcal{F}})|$

$$\langle\Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(0)}\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(0)}\rangle$$
$$= E_0^{(0)}\langle\Psi_0^{(1)}(\vec{\mathcal{F}}) \mid \Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + E_0^{(1)}(\vec{\mathcal{F}})\langle\Psi_0^{(1)}(\vec{\mathcal{F}}) \mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle + E_0^{(2)}(\vec{\mathcal{F}})\langle\Psi_0^{(1)}(\vec{\mathcal{F}}) \mid \Psi_0^{(0)}\rangle$$

Using again the intermediate normalization and rearranging we obtain

$$\begin{aligned}\langle \Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,E_0^{(0)} - \hat{H}^{(0)}\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle = \langle \Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle \\ -\; E_0^{(1)}(\vec{\mathcal{F}})\langle \Psi_0^{(1)}(\vec{\mathcal{F}})\mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle \\ +\; \langle \Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(2)}(\vec{\mathcal{F}})\,|\,\Psi_0^{(0)}\rangle\end{aligned}$$

Going back this means that $\langle \Psi_0^{(0)}\,|\,\hat{H}^{(1)}(\vec{\mathcal{F}})\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle$ can be rewritten as

$$\begin{aligned}\langle \Psi_0^{(0)}\,|\,\hat{H}^{(1)}(\vec{\mathcal{F}})\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle &= \langle \Psi_0^{(2)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(0)}\rangle^* \\ &= \langle \Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,E_0^{(0)} - \hat{H}^{(0)}\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle \\ &= \langle \Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle \\ &\quad -\; E_0^{(1)}(\vec{\mathcal{F}})\langle \Psi_0^{(1)}(\vec{\mathcal{F}})\mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle \\ &\quad +\; \langle \Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(0)}\rangle\end{aligned}$$

and that the third-order energy correction can alternatively be written as

$$\begin{aligned}E_0^{(3)}(\vec{\mathcal{F}}) &= \langle \Psi_0^{(0)}\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(2)}(\vec{\mathcal{F}})\rangle + \langle \Psi_0^{(0)}\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle \\ &= \langle \Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(1)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle -\; E_0^{(1)}(\vec{\mathcal{F}})\langle \Psi_0^{(1)}(\vec{\mathcal{F}})\mid \Psi_0^{(1)}(\vec{\mathcal{F}})\rangle \\ &\quad +\; \langle \Psi_0^{(1)}(\vec{\mathcal{F}})\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(0)}\rangle + \langle \Psi_0^{(0)}\,|\,\hat{H}^{(2)}\,|\,\Psi_0^{(1)}(\vec{\mathcal{F}})\rangle\end{aligned}$$

showing that it only depends on the zeroth and first order wavefunction in agreement with the $2m+1$ rule

3.6 Deriving Eq. (3.81) starting from Eq. (3.80):

$$\imath\hbar\frac{\partial}{\partial t}|\Psi_0^I(t,\vec{\mathcal{F}})\rangle = -\hat{H}^{(0)}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}|\Psi_0(t,\vec{\mathcal{F}})\rangle + e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\imath\hbar\frac{\partial}{\partial t}|\Psi_0(t,\vec{\mathcal{F}})\rangle$$

The time derivative $\imath\hbar\frac{\partial}{\partial t}$ of $|\Psi_0(t,\vec{\mathcal{F}})\rangle$ is known from the electronic Schrödinger equation, Eq. (3.74):

$$\imath\hbar\frac{\partial}{\partial t}|\Psi_0(t,\vec{\mathcal{F}})\rangle = \left(\hat{H}^{(0)} + \hat{H}^{(1)}(t)\right)|\Psi_0(t,\vec{\mathcal{F}})\rangle$$

Inserting this we obtain

$$\begin{aligned}\imath\hbar\frac{\partial}{\partial t}|\Psi_0^I(t,\vec{\mathcal{F}})\rangle &= -\hat{H}^{(0)}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}|\Psi_0(t,\vec{\mathcal{F}})\rangle + e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\left(\hat{H}^{(0)} + \hat{H}^{(1)}(t)\right)|\Psi_0(t,\vec{\mathcal{F}})\rangle \\ &= -\hat{H}^{(0)}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}|\Psi_0(t,\vec{\mathcal{F}})\rangle + e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{H}^{(0)}|\Psi_0(t,\vec{\mathcal{F}})\rangle \\ &\quad + e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{H}^{(1)}(t)|\Psi_0(t,\vec{\mathcal{F}})\rangle\end{aligned}$$

And, because $\left[e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}, \hat{H}^{(0)}\right] = 0$, we can write:

$$\begin{aligned}
\imath\hbar\frac{\partial}{\partial t}|\Psi_0^I(t,\vec{\mathcal{F}})\rangle &= -e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{H}^{(0)}|\Psi_0(t,\vec{\mathcal{F}})\rangle + e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\left(\hat{H}^{(0)} + \hat{H}^{(1)}(t)\right)|\Psi_0(t,\vec{\mathcal{F}})\rangle \\
&= e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{H}^{(1)}(t)|\Psi_0(t,\vec{\mathcal{F}})\rangle \\
&= e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{H}^{(1)}(t)e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}|\Psi_0(t,\vec{\mathcal{F}})\rangle \\
&= \hat{H}^{(1),I}(t)|\Psi_0^I(t,\vec{\mathcal{F}})\rangle
\end{aligned}$$

3.7 As shown below, the linear response function only depends on a time interval $t - t'$ and not on the two absolute times, t and t'

$$\begin{aligned}
\langle\langle\hat{P}^I(t);\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t')\rangle\rangle &= \Theta(t-t')\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\left[\hat{P}^I(t),\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t')\right]|\Psi_0^{(0)}\rangle \\
&= \Theta(t-t')\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\Big[e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{P}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t'}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t'} \\
&\quad - e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t'}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t'}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{P}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}\Big]|\Psi_0^{(0)}\rangle \\
&= \Theta(t-t')\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\Big[e^{\frac{\imath}{\hbar}E_0^{(0)}t}\hat{P}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}(t'-t)}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}E_0^{(0)}t'} \\
&\quad - e^{\frac{\imath}{\hbar}E_0^{(0)}t'}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}(t'-t)}\hat{P}e^{-\frac{\imath}{\hbar}E_0^{(0)}t}\Big]|\Psi_0^{(0)}\rangle
\end{aligned}$$

where we have used that $|\Psi_0^{(0)}\rangle$ is an eigenfunction of the unperturbed Hamiltonian with eigenvalue $E_0^{(0)}$ which implies that

$$e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}|\Psi_0^{(0)}\rangle = \sum_n \frac{1}{n!}\left(\frac{\imath}{\hbar}\hat{H}^{(0)}t\right)^n|\Psi_0^{(0)}\rangle = \sum_n \frac{1}{n!}\left(\frac{\imath}{\hbar}E_0^{(0)}t\right)^n|\Psi_0^{(0)}\rangle = e^{\frac{\imath}{\hbar}E_0^{(0)}t}|\Psi_0^{(0)}\rangle$$

and likewise for the complex conjugate. Using the fact that $e^{\frac{\imath}{\hbar}E_0^{(0)}t}$ is a function (and not an operator), and thus, commutes with all the operators, we obtain

$$\begin{aligned}
\langle\langle\hat{P}^I(t);\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t')\rangle\rangle &= \Theta(t-t')\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\Big[\hat{P}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}(t'-t)}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}E_0^{(0)}(t'-t)} \\
&\quad - e^{\frac{\imath}{\hbar}E_0^{(0)}(t'-t)}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}(t'-t)}\hat{P}\Big]|\Psi_0^{(0)}\rangle \\
&= \Theta(t-t')\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\Big[\hat{P}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}(t'-t)}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}(t'-t)} \\
&\quad - e^{\frac{\imath}{\hbar}\hat{H}^{(0)}(t'-t)}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}(t'-t)}\hat{P}\Big]|\Psi_0^{(0)}\rangle \\
&= \Theta(t-t')\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\left[\hat{P}\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t'-t) - \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t'-t)\hat{P}\right]|\Psi_0^{(0)}\rangle
\end{aligned}$$

or

$$\langle\langle \hat{P}^I(t); \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t')\rangle\rangle = \Theta(t-t')\frac{1}{\imath\hbar}\langle\Psi^{(0)}_0|\Big[\hat{P}, \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t'-t)\Big]|\Psi^{(0)}_0\rangle$$
$$= \langle\langle \hat{P}; \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t'-t)\rangle\rangle$$

<u>3.8</u> The linear response function in the time domain reads, Eq. (3.107),

$$\langle\langle \hat{P}; \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t)\rangle\rangle = \Theta(-t)\frac{1}{\imath\hbar}\langle\Psi^{(0)}_0|\Big[\hat{P}, \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t)\Big]|\Psi^{(0)}_0\rangle$$

where t now denotes a time interval. The eigenfunctions of the unperturbed Hamiltonian form a complete set and we use this to invoke the resolution of the identity, i.e.

$$1 = \sum_n |\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n|$$

This gives

$$\begin{aligned}
\langle\langle \hat{P}; \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t)\rangle\rangle =& \Theta(-t)\frac{1}{\imath\hbar}\langle\Psi^{(0)}_0|\hat{P}\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t) - \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t)\hat{P}|\Psi^{(0)}_0\rangle \\
=& \Theta(-t)\frac{1}{\imath\hbar}\sum_n\Big[\langle\Psi^{(0)}_0|\hat{P}|\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n|\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t)|\Psi^{(0)}_0\rangle \\
&- \langle\Psi^{(0)}_0|\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t)|\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n|\hat{P}|\Psi^{(0)}_0\rangle\Big] \\
=& \Theta(-t)\frac{1}{\imath\hbar}\sum_n\Big[\langle\Psi^{(0)}_0|\hat{P}|\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n|e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}|\Psi^{(0)}_0\rangle \\
&- \langle\Psi^{(0)}_0|e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}|\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n|\hat{P}|\Psi^{(0)}_0\rangle\Big] \\
=& \Theta(-t)\frac{1}{\imath\hbar}\sum_n\Big[\langle\Psi^{(0)}_0|\hat{P}|\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n|e^{\frac{\imath}{\hbar}E^{(0)}_n t}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}E^{(0)}_0 t}|\Psi^{(0)}_0\rangle \\
&- \langle\Psi^{(0)}_0|e^{\frac{\imath}{\hbar}E^{(0)}_0 t}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}E^{(0)}_n t}|\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n|\hat{P}|\Psi^{(0)}_0\rangle\Big] \\
=& \Theta(-t)\frac{1}{\imath\hbar}\sum_n\Big[\langle\Psi^{(0)}_0|\hat{P}|\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n|\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}(E^{(0)}_0-E^{(0)}_n)t}|\Psi^{(0)}_0\rangle \\
&- \langle\Psi^{(0)}_0|\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{\frac{\imath}{\hbar}(E^{(0)}_0-E^{(0)}_n)t}|\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n|\hat{P}|\Psi^{(0)}_0\rangle\Big]
\end{aligned}$$

Performing the Fourier transformation of the response function

$$\langle\langle \hat{P}; \hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_\omega = \int_{-\infty}^{\infty}\langle\langle \hat{P}; \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t)\rangle\rangle e^{-\imath\omega t}dt$$

we obtain

$$\langle\langle \hat{P}; \hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_\omega = \frac{1}{\imath\hbar}\sum_n \int_{-\infty}^{\infty} \Theta(-t)\Big[\langle\Psi_0^{(0)}|\hat{P}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}^{\omega}_{\beta\ldots} e^{-\frac{\imath}{\hbar}(E_0^{(0)}-E_n^{(0)}+\hbar\omega)t}|\Psi_0^{(0)}\rangle$$

$$- \langle\Psi_0^{(0)}|\hat{O}^{\omega}_{\beta\ldots} e^{\frac{\imath}{\hbar}(E_0^{(0)}-E_n^{(0)}-\hbar\omega)t}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{P}|\Psi_0^{(0)}\rangle\Big] dt$$

$$= \frac{1}{\imath\hbar}\sum_n \Big[\langle\Psi_0^{(0)}|\hat{P}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_0^{(0)}\rangle \int_{-\infty}^{\infty} \Theta(-t) e^{-\frac{\imath}{\hbar}(E_0^{(0)}-E_n^{(0)}+\hbar\omega)t} dt$$

$$- \langle\Psi_0^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{P}|\Psi_0^{(0)}\rangle \int_{-\infty}^{\infty} \Theta(-t) e^{\frac{\imath}{\hbar}(E_0^{(0)}-E_n^{(0)}-\hbar\omega)t} dt\Big]$$

Change of integration variable $x = -t$ (the limits of integration have been changed accordingly, however, subsequently they have been interchanged by changing the sign of the integral) gives

$$\langle\langle \hat{P}; \hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_\omega = \frac{1}{\hbar}\sum_n \Big[\langle\Psi_0^{(0)}|\hat{P}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_0^{(0)}\rangle \frac{1}{\imath}\int_{-\infty}^{\infty} \Theta(x) e^{\frac{\imath}{\hbar}(E_0^{(0)}-E_n^{(0)}+\hbar\omega)x} dx$$

$$- \langle\Psi_0^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{P}|\Psi_0^{(0)}\rangle \frac{1}{\imath}\int_{-\infty}^{\infty} \Theta(x) e^{-\frac{\imath}{\hbar}(E_0^{(0)}-E_n^{(0)}-\hbar\omega)x} dx\Big]$$

Using that

$$\frac{1}{\imath}\int_{-\infty}^{\infty} e^{\imath a t}\Theta(t) dt = \lim_{\eta\to 0^+}\int_{-\infty}^{\infty}\frac{\delta(a-x)}{x+\imath\eta} dx = \lim_{\eta\to 0^+}\frac{1}{a+\imath\eta} = \frac{1}{a}$$

with $a = \hbar^{-1}(E_0^{(0)} - E_n^{(0)} + \hbar\omega)$ in the first integral and $a = -\hbar^{-1}(E_0^{(0)} - E_n^{(0)} - \hbar\omega)$ in the second, we arrive at

$$\langle\langle \hat{P}; \hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_\omega = \sum_n \left[\frac{\langle\Psi_0^{(0)}|\hat{P}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)} + \hbar\omega} + \frac{\langle\Psi_0^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{P}|\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)} - \hbar\omega}\right]$$

The contribution from $n = 0$ is

$$\frac{\langle\Psi_0^{(0)}|\hat{P}|\Psi_0^{(0)}\rangle\langle\Psi_0^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_0^{(0)} + \hbar\omega} + \frac{\langle\Psi_0^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_0^{(0)}\rangle\langle\Psi_0^{(0)}|\hat{P}|\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_0^{(0)} - \hbar\omega} = 0$$

and hence $n = 0$ can safely be omitted in the summation thereby giving Eq. (3.110)

$$\langle\langle \hat{P}; \hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_\omega = \sum_{n\neq 0} \left[\frac{\langle\Psi_0^{(0)}|\hat{P}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)} + \hbar\omega} + \frac{\langle\Psi_0^{(0)}|\hat{O}^{\omega}_{\beta\ldots}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{P}|\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)} - \hbar\omega}\right]$$

3.9 The second-order correction to the time-dependent expectation value of $\hat{P}$ reads

$$\begin{aligned}\langle\Psi_0(t,\vec{\mathcal{F}})|\hat{P}|\Psi_0(t,\vec{\mathcal{F}})\rangle^{(2)} =& \langle\Psi_0^{(1)}(t,\vec{\mathcal{F}})|\hat{P}|\Psi_0^{(1)}(t,\vec{\mathcal{F}})\rangle \\ &+ \langle\Psi_0^{(0)}(t,\vec{\mathcal{F}})|\hat{P}|\Psi_0^{(2)}(t,\vec{\mathcal{F}})\rangle + \langle\Psi_0^{(2)}(t,\vec{\mathcal{F}})|\hat{P}|\Psi_0^{(0)}(t,\vec{\mathcal{F}})\rangle\end{aligned}$$

where according to Eq. (3.87) and Eq. (3.88) the first- and second-order correction to the time-dependent wavefunction are given as

$$\begin{aligned}|\Psi_0^{(1)}(t,\vec{\mathcal{F}})\rangle =& \frac{1}{\imath\hbar}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}\int_{-\infty}^{t} dt'\hat{H}^{(1),I}(t')|\Psi_0^{(0)}\rangle \\ |\Psi_0^{(2)}(t,\vec{\mathcal{F}})\rangle =& \left(\frac{1}{\imath\hbar}\right)^2 e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}\int_{-\infty}^{t} dt'\int_{-\infty}^{t'} dt''\hat{H}^{(1),I}(t')\hat{H}^{(1),I}(t'')|\Psi_0^{(0)}\rangle\end{aligned}$$

and their adjoints are

$$\begin{aligned}\langle\Psi_0^{(1)}(t,\vec{\mathcal{F}})| =& \frac{\imath}{\hbar}\langle\Psi_0^{(0)}|\int_{-\infty}^{t} dt'\hat{H}^{(1),I}(t')e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t} \\ \langle\Psi_0^{(2)}(t,\vec{\mathcal{F}})| =& \left(\frac{1}{\imath\hbar}\right)^2\langle\Psi_0^{(0)}|\int_{-\infty}^{t} dt'\int_{-\infty}^{t'} dt''\hat{H}^{(1),I}(t')\hat{H}^{(1),I}(t'')e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\end{aligned}$$

using the Hermiticity of $\hat{H}^{(0)}$ and $(\hat{H}^{(1),I})^\dagger = (e^{\frac{\imath}{\hbar}\hat{H}(0)t}\hat{H}^{(1)}e^{-\frac{\imath}{\hbar}\hat{H}(0)t})^\dagger = \hat{H}^{(1),I}$. Inserting the expressions for the first- and second-order corrections to the wavefunction into the second-order correction to the expectation value, we obtain for the first term

$$\begin{aligned}&\langle\Psi_0^{(1)}(t,\vec{\mathcal{F}})\,|\,\hat{P}\,|\,\Psi_0^{(1)}(t,\vec{\mathcal{F}})\rangle \\ &\quad= -\left(\frac{1}{\imath\hbar}\right)^2\int_{-\infty}^{t} dt'\int_{-\infty}^{t} dt''\langle\Psi_0^{(0)}\,|\,\hat{H}^{(1),I}(t')e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{P}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{H}^{(1),I}(t'')\,|\,\Psi_0^{(0)}\rangle \\ &\quad= -\left(\frac{1}{\imath\hbar}\right)^2\int_{-\infty}^{t} dt'\int_{-\infty}^{t} dt''\langle\Psi_0^{(0)}\,|\,\hat{H}^{(1),I}(t')\hat{P}^I\hat{H}^{(1),I}(t'')\,|\,\Psi_0^{(0)}\rangle\end{aligned}$$

The function is symmetric with respect to t' and t'' and we can therefore rewrite the expression as,

$$\begin{aligned}&= -2\left(\frac{1}{\imath\hbar}\right)^2\int_{-\infty}^{t} dt'\int_{-\infty}^{t'} dt''\langle\Psi_0^{(0)}\,|\,\hat{H}^{(1),I}(t')\hat{P}^I\hat{H}^{(1),I}(t'')\,|\,\Psi_0^{(0)}\rangle \\ &= -\left(\frac{1}{\imath\hbar}\right)^2\int_{-\infty}^{t} dt'\int_{-\infty}^{t'} dt''\Big(\langle\Psi_0^{(0)}\,|\,\hat{H}^{(1),I}(t')\hat{P}^I\hat{H}^{(1),I}(t'')\,|\,\Psi_0^{(0)}\rangle \\ &\qquad + \langle\Psi_0^{(0)}\,|\,\hat{H}^{(1),I}(t'')\hat{P}^I\hat{H}^{(1),I}(t')\,|\,\Psi_0^{(0)}\rangle\Big)\end{aligned}$$

where t'' now is integrated from $-\infty$ to t'.

The second term becomes

$$
\begin{aligned}
&\langle\Psi_0^{(0)}(t,\vec{\mathcal{F}})|\hat{P}|\Psi_0^{(2)}(t,\vec{\mathcal{F}})\rangle \\
&= \left(\frac{1}{\imath\hbar}\right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \langle\Psi_0^{(0)}(t,\vec{\mathcal{F}})|\hat{P}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{H}^{(1),I}(t')\hat{H}^{(1),I}(t'')|\Psi_0^{(0)}\rangle \\
&= \left(\frac{1}{\imath\hbar}\right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \langle\Psi_0^{(0)}|e^{\frac{\imath}{\hbar}\hat{H}^{(0)}}\hat{P}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{H}^{(1),I}(t')\hat{H}^{(1),I}(t'')|\Psi_0^{(0)}\rangle \\
&= \left(\frac{1}{\imath\hbar}\right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \langle\Psi_0^{(0)}|\hat{P}^I(t)\hat{H}^{(1),I}(t')\hat{H}^{(1),I}(t'')|\Psi_0^{(0)}\rangle
\end{aligned}
$$

while for the third term, we have

$$
\begin{aligned}
&\langle\Psi_0^{(2)}(t,\vec{\mathcal{F}})|\hat{P}|\Psi_0^{(0)}(t,\vec{\mathcal{F}})\rangle \\
&= \left(\frac{1}{\imath\hbar}\right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \langle\Psi_0^{(0)}|\hat{H}^{(1),I}(t'')\hat{H}^{(1),I}(t')e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{P}|\Psi_0^{(0)}(t,\vec{\mathcal{F}})\rangle \\
&= \left(\frac{1}{\imath\hbar}\right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \langle\Psi_0^{(0)}|\hat{H}^{(1),I}(t'')\hat{H}^{(1),I}(t')e^{\frac{\imath}{\hbar}\hat{H}^{(0)}}\hat{P}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}|\Psi_0^{(0)}\rangle \\
&= \left(\frac{1}{\imath\hbar}\right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \langle\Psi_0^{(0)}|\hat{H}^{(1),I}(t'')\hat{H}^{(1),I}(t')\hat{P}^I(t)|\Psi_0^{(0)}\rangle
\end{aligned}
$$

where we have used that $|\Psi_0^{(0)}(t,\vec{\mathcal{F}})\rangle = e^{-\frac{\imath}{\hbar}E_0^{(0)}t}|\Psi_0^{(0)}\rangle = e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}|\Psi_0^{(0)}\rangle$. Finally collecting the three terms and recognizing the double nested commutator, we arrive at

$$
\begin{aligned}
&\langle\Psi_0(t,\vec{\mathcal{F}})|\hat{P}|\Psi_0(t,\vec{\mathcal{F}})\rangle^{(2)} \\
&= \left(\frac{1}{\imath\hbar}\right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \langle\Psi_0^{(0)}|\Big[\hat{P}^I(t)\hat{H}^{(1),I}(t')\hat{H}^{(1),I}(t'') \\
&\qquad + \hat{H}^{(1),I}(t'')\hat{H}^{(1),I}(t')\hat{P}^I(t) - \hat{H}^{(1),I}(t')\hat{P}^I(t)\hat{H}^{(1),I}(t'') \\
&\qquad - \hat{H}^{(1),I}(t'')\hat{P}^I(t)\hat{H}^{(1),I}(t')\Big]|\Psi_0^{(0)}\rangle \\
&= \left(\frac{1}{\imath\hbar}\right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \langle\Psi_0^{(0)}|\Big[\big[\hat{P}^I(t),\hat{H}^{(1),I}(t')\big],\hat{H}^{(1),I}(t'')\Big]|\Psi_0^{(0)}\rangle
\end{aligned}
$$

This is Eq. (3.120) and can be turned in to Eq. (3.121) by using the heaviside step function.

3.10 Using the fact that the perturbation operator in the Schrödinger picture $\hat{O}^{\mathcal{F}}_{\beta\ldots}$ is independent of time and that $[e^{\pm\frac{\imath}{\hbar}\hat{H}^{(0)}t},\hat{H}^{(0)}] = 0$, we show below that the time derivative of an operator in the Interaction picture is the commutator of the operator with the Hamiltonian, i.e.

$$\begin{aligned}
\frac{d}{dt}\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t) &= \frac{d}{dt}\left(e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}O^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}\right) \\
&= \left(\frac{d}{dt}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\right)\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t} + e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{O}^{\mathcal{F}}_{\beta\ldots}\left(\frac{d}{dt}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}\right) \\
&= \frac{\imath}{\hbar}\hat{H}^{(0)}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t} - \frac{\imath}{\hbar}e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{O}^{\mathcal{F}}_{\beta\ldots}\hat{H}^{(0)}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t} \\
&= \frac{\imath}{\hbar}\left[\hat{H}^{(0)}\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t) - e^{\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{O}^{\mathcal{F}}_{\beta\ldots}e^{-\frac{\imath}{\hbar}\hat{H}^{(0)}t}\hat{H}^{(0)}\right] \\
&= \frac{\imath}{\hbar}\left[\hat{H}^{(0)}\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t) - \hat{O}^{\mathcal{F},I}_{\beta\ldots}(t)\hat{H}^{(0)}\right] \\
&= \frac{1}{\imath\hbar}\left[\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t), \hat{H}^{(0)}\right]
\end{aligned}$$

3.11 The equation of motion of the linear response function in the time domain, Eq. (3.133) , reads

$$\imath\hbar\frac{d}{dt}\langle\langle\hat{P},\hat{O}^{\mathcal{F},I(t)}_{\beta\ldots}\rangle\rangle = -\delta(t)\langle\Psi^{(0)}_0|[\hat{P},\hat{O}^{\mathcal{F}}_{\beta\ldots}]|\Psi^{(0)}_0\rangle - \langle\langle\hat{P};[\hat{H}^{(0)},\hat{O}^{\mathcal{F},I}_{\beta\ldots}(t)]\rangle\rangle$$

Using the inverse Fourier transform of the linear response function, Eq. (3.135),

$$\langle\langle\hat{P},\hat{O}^{\mathcal{F},I(t)}_{\beta\ldots}\rangle\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\ \langle\langle\hat{P};\hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_\omega e^{\imath\omega t}$$

and the definition of the Dirac Delta function as the inverse Fourier transform of 1, i.e. Eq. (3.136)

$$\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty}e^{\imath\omega t}d\omega$$

the equation of motion can be rewritten according to

$$\begin{aligned}
\imath\hbar\frac{1}{2\pi}\frac{d}{dt}\int_{-\infty}^{\infty}d\omega\ \langle\langle\hat{P};\hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_\omega e^{\imath\omega t} = &-\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{\imath\omega t}d\omega\langle\Psi^{(0)}_0|[\hat{P},\hat{O}^{\omega}_{\beta\ldots}]|\Psi^{(0)}_0\rangle \\
&-\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\ \langle\langle\hat{P};[\hat{H}^{(0)},\hat{O}^{\omega}_{\beta\ldots}]\rangle\rangle_\omega e^{\imath\omega t}
\end{aligned}$$

The order of differentiation and integration can be interchanged on the l.h.s., because they are with respect to different variables

$$\begin{aligned}
\int_{-\infty}^{\infty}d\omega\ \imath\hbar\frac{d}{dt}\left(\langle\langle\hat{P};\hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_\omega e^{\imath\omega t}\right) = &-\int_{-\infty}^{\infty}e^{\imath\omega t}d\omega\langle\Psi^{(0)}_0|[\hat{P},\hat{O}^{\omega}_{\beta\ldots}]|\Psi^{(0)}_0\rangle \\
&-\int_{-\infty}^{\infty}d\omega\ \langle\langle\hat{P};[\hat{H}^{(0)},\hat{O}^{\omega}_{\beta\ldots}]\rangle\rangle_\omega e^{\imath\omega t}
\end{aligned}$$

Subsequently, we remove the integration over the frequencies which occurs on both sides of the equality and obtain

$$\imath\hbar\frac{d}{dt}\left(\langle\langle\hat{P};\hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_{\omega}e^{\imath\omega t}\right) = -\, e^{\imath\omega t}\langle\Psi_0^{(0)}|[\hat{P},\hat{O}^{\omega}_{\beta\ldots}]|\Psi_0^{(0)}\rangle - \langle\langle\hat{P};[\hat{H}^{(0)},\hat{O}^{\omega}_{\beta\ldots}]\rangle\rangle_{\omega}e^{\imath\omega t}$$

or after differentation

$$\imath\hbar\ \langle\langle\hat{P};\hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_{\omega}\ (\imath\omega)e^{\imath\omega t} = -\, e^{\imath\omega t}\langle\Psi_0^{(0)}|[\hat{P},\hat{O}^{\omega}_{\beta\ldots}]|\Psi_0^{(0)}\rangle - \langle\langle\hat{P};[\hat{H}^{(0)},\hat{O}^{\omega}_{\beta\ldots}]\rangle\rangle_{\omega}e^{\imath\omega t}$$

Finally, elimination of the exponentials yields the equation of motion of the linear response function in the frequency domain, Eq. (3.134),

$$\hbar\omega\ \langle\langle\hat{P};\hat{O}^{\omega}_{\beta\ldots}\rangle\rangle_{\omega}\ = \langle\Psi_0^{(0)}|[\hat{P},\hat{O}^{\omega}_{\beta\ldots}]|\Psi_0^{(0)}\rangle + \langle\langle\hat{P};[\hat{H}^{(0)},\hat{O}^{\omega}_{\beta\ldots}]\rangle\rangle_{\omega}$$

3.12 If one chooses the state-transfer operators to be, Eq. (3.165),

$$\{\hat{h}_n\} = \left\{{}^{e}\hat{h}_n, {}^{d}\,\hat{h}_n\right\} = \left\{|\Psi_n^{(0)}\rangle\langle\Psi_0^{(0)}|, |\Psi_0^{(0)}\rangle\langle\Psi_n^{(0)}|\right\}$$

the overlap matrix and electronic Hessian matrix become diagonal, i.e. the off-diagonal blocks of the overlap matrix ${}^{ed}\boldsymbol{S}$ and ${}^{de}\boldsymbol{S}$, and the electronic Hessian matrix, ${}^{ed}\boldsymbol{E}$ and ${}^{de}\boldsymbol{E}$, vanish in this basis. For the off-diagonal blocks of the overlap matrix, we have

$$\begin{aligned}
{}^{ed}\mathbf{S}_{ij} &= \langle\Psi_0^{(0)}|\left[\left(|\Psi_i^{(0)}\rangle\langle\Psi_0^{(0)}|\right)^{\dagger}, |\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\right]|\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|\left[|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|, |\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\right]|\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|\Psi_0^{(0)}\rangle \\
&= 0
\end{aligned}$$

and

$$\begin{aligned}
{}^{de}\mathbf{S}_{ij} &= \langle\Psi_0^{(0)}|\left[\left(|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|\right)^{\dagger}, |\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\right]|\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|\left[|\Psi_i^{(0)}\rangle\langle\Psi_0^{(0)}|, |\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\right]|\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_i^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle \\
&= 0
\end{aligned}$$

where we have used the orthonormality of the states, recalling that $i, j \neq 0$.

For the electronic Hessian matrix, we have

$$
\begin{aligned}
{}^{ed}\mathbf{E}_{ij} &= \langle\Psi_0^{(0)}| \left[\left(|\Psi_i^{(0)}\rangle\langle\Psi_0^{(0)}|\right)^\dagger, \left[\hat{H}^{(0)}, |\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\right]\right] |\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}| \left[|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|, \left(\hat{H}^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}| - |\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\hat{H}^{(0)}\right)\right] |\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|\hat{H}^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\hat{H}^{(0)}|\Psi_0^{(0)}\rangle \\
&\quad - \langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|\Psi_0^{(0)}\rangle + \langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_j^{(0)}|\hat{H}^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|\Psi_0^{(0)}\rangle \\
&= 0
\end{aligned}
$$

and

$$
\begin{aligned}
{}^{de}\mathbf{E}_{ij} &= \langle\Psi_0^{(0)}| \left[\left(|\Psi_0^{(0)}\rangle\langle\Psi_i^{(0)}|\right)^\dagger, \left[\hat{H}^{(0)}, |\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\right]\right] |\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}| \left[|\Psi_i^{(0)}\rangle\langle\Psi_0^{(0)}|, \left(\hat{H}^{(0)}|\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}| - |\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\hat{H}^{(0)}\right)\right] |\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|\Psi_i^{(0)}\rangle\langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|\Psi_i^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_0^{(0)}\rangle \\
&\quad - \langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_i^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle + \langle\Psi_0^{(0)}|\Psi_j^{(0)}\rangle\langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_i^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle \\
&= 0
\end{aligned}
$$

3.13 If one chooses the state-transfer operators as, Eq. (3.165),

$$
\{\hat{h}_n\} = \left\{{}^e\hat{h}_n, {}^d\hat{h}_n\right\} = \left\{|\Psi_n^{(0)}\rangle\langle\Psi_0^{(0)}|, |\Psi_0^{(0)}\rangle\langle\Psi_n^{(0)}|\right\},
$$

the diagonal blocks of the overlap and electronic Hessian matrices are themself diagonal. To show this we use the following identities

$$
\begin{aligned}
{}^{ee}\mathbf{S}_{nm} &= \langle\Psi_0^{(0)}| \left[{}^e\hat{h}_n^\dagger, {}^e\hat{h}_m\right] |\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}| \left[{}^d\hat{h}_n {}^e\hat{h}_m - {}^e\hat{h}_m {}^d\hat{h}_n\right] |\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}|{}^d\hat{h}_n {}^e\hat{h}_m|\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|{}^e\hat{h}_n^\dagger {}^e\hat{h}_m|\Psi_0^{(0)}\rangle \\
{}^{dd}\mathbf{S}_{nm} &= \langle\Psi_0^{(0)}| \left[{}^d\hat{h}_n^\dagger, {}^d\hat{h}_m\right] |\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}| \left[{}^e\hat{h}_n {}^d\hat{h}_m - {}^d\hat{h}_m {}^e\hat{h}_n\right] |\Psi_0^{(0)}\rangle = -\langle\Psi_0^{(0)}|{}^d\hat{h}_n {}^e\hat{h}_m|\Psi_0^{(0)}\rangle \\
&= -\langle\Psi_0^{(0)}|{}^d\hat{h}_n {}^d\hat{h}_m^\dagger|\Psi_0^{(0)}\rangle \\
{}^{ee}\mathbf{E}_{nm} &= \langle\Psi_0^{(0)}| \left[{}^e\hat{h}_n^\dagger, \left[\hat{H}^{(0)}, {}^e\hat{h}_m\right]\right] |\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}|{}^d\hat{h}_n \left[\hat{H}^{(0)}, {}^e\hat{h}_m\right] |\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|{}^e\hat{h}_n^\dagger \left[\hat{H}^{(0)}, {}^e\hat{h}_m\right] |\Psi_0^{(0)}\rangle \\
{}^{dd}\mathbf{E}_{nm} &= \langle\Psi_0^{(0)}| \left[{}^d\hat{h}_n^\dagger, \left[\hat{H}^{(0)}, {}^d\hat{h}_m\right]\right] |\Psi_0^{(0)}\rangle = -\langle\Psi_0^{(0)}| \left[\hat{H}^{(0)}, {}^d\hat{h}_m\right] {}^e\hat{h}_n|\Psi_0^{(0)}\rangle \\
&= -\langle\Psi_0^{(0)}| \left[\hat{H}^{(0)}, {}^d\hat{h}_m\right] {}^d\hat{h}_n^\dagger|\Psi_0^{(0)}\rangle
\end{aligned}
$$

To derive these, we have used the fact that the deexcitation operators are the hermitian conjugate of the excitation operators ${}^e\hat{h}_n^\dagger = {}^d\hat{h}_n$ as well as the killer condition ${}^{d}\hat{h}_n|\Psi_0^{(0)}\rangle = 0$. The elements of the diagonal blocks of the overlap matrix are

$$
\begin{aligned}
{}^{ee}\mathbf{S}_{nm} &= \langle\Psi_0^{(0)}|(|\Psi_n^{(0)}\rangle\langle\Psi_0^{(0)}|)^\dagger|\Psi_m^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_n^{(0)}|\Psi_m^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle \\
&= \delta_{nm}
\end{aligned}
$$

and

$$
\begin{aligned}
{}^{dd}\mathbf{S}_{nm} &= -\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_n^{(0)}|(|\Psi_0^{(0)}\rangle\langle\Psi_m^{(0)}|)^\dagger|\Psi_0^{(0)}\rangle = -\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_n^{(0)}|\Psi_m^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle \\
&= -\delta_{nm}
\end{aligned}
$$

The elements of the corresponding blocks in the electronic Hessian matrix are

$$
\begin{aligned}
{}^{ee}\mathbf{E}_{nm} &= \langle\Psi_0^{(0)}|\left(|\Psi_n^{(0)}\rangle\langle\Psi_0^{(0)}|\right)^\dagger\left[\hat{H}^{(0)}, |\Psi_m^{(0)}\rangle\langle\Psi_0^{(0)}|\right]|\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|\left(|\Psi_0^{(0)}\rangle\langle\Psi_n^{(0)}|\left[\hat{H}^{(0)}, |\Psi_m^{(0)}\rangle\langle\Psi_0^{(0)}|\right]\right)|\Psi_0^{(0)}\rangle \\
&= \langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{H}^{(0)}|\Psi_m^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_n^{(0)}|\Psi_m^{(0)}\rangle\langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_0^{(0)}\rangle \\
&= \delta_{nm}(E_n^{(0)} - E_0^{(0)})
\end{aligned}
$$

and

$$
\begin{aligned}
{}^{dd}\mathbf{E}_{nm} &= -\langle\Psi_0^{(0)}|\left[\hat{H}^{(0)}, |\Psi_0^{(0)}\rangle\langle\Psi_m^{(0)}|\right]\left(|\Psi_0^{(0)}\rangle\langle\Psi_n^{(0)}|\right)^\dagger|\Psi_0^{(0)}\rangle \\
&= -\langle\Psi_0^{(0)}|\left(\left[\hat{H}^{(0)}, |\Psi_0^{(0)}\rangle\langle\Psi_m^{(0)}|\right]|\Psi_n^{(0)}\rangle\langle\Psi_0^{(0)}|\right)|\Psi_0^{(0)}\rangle \\
&= -\langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_m^{(0)}|\Psi_n^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle + \langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle\langle\Psi_m^{(0)}|\hat{H}^{(0)}|\Psi_n^{(0)}\rangle\langle\Psi_0^{(0)}|\Psi_0^{(0)}\rangle \\
&= \delta_{nm}(E_n^{(0)} - E_0^{(0)})
\end{aligned}
$$

Analogously, for the property gradient vectors

$$
{}^{e}\mathbf{T}_n^T(\hat{P}) = \langle\Psi_0^{(0)}|[\hat{P}, {}^{e}\hat{h}_n]|\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}|\hat{P}\ {}^{e}\hat{h}_n|\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}|\hat{P}|\Psi_n^{(0)}\rangle
$$

$$
{}^{d}\mathbf{T}_n^T(\hat{P}) = \langle\Psi_0^{(0)}|[\hat{P}, {}^{d}\hat{h}_n]|\Psi_0^{(0)}\rangle = -\langle\Psi_0^{(0)}|{}^{d}\hat{h}_n\hat{P}|\Psi_0^{(0)}\rangle = -\langle\Psi_n^{(0)}|\hat{P}|\Psi_0^{(0)}\rangle
$$

$$
\begin{aligned}
{}^{e}\mathbf{T}_n^T(\hat{O}^\omega_{\beta\ldots}) &= \langle\Psi_0^{(0)}|[{}^{e}\hat{h}_n^\dagger, \hat{O}^\omega_{\beta\ldots}]|\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}|[{}^{d}\hat{h}_n, \hat{O}^\omega_{\beta\ldots}]|\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}|{}^{d}\hat{h}_n\hat{O}^\omega_{\beta\ldots}|\Psi_0^{(0)}\rangle \\
&= \langle\Psi_n^{(0)}|\hat{O}^\omega_{\beta\ldots}|\Psi_0^{(0)}\rangle
\end{aligned}
$$

$$
\begin{aligned}
{}^{d}\mathbf{T}_n^T(\hat{O}^\omega_{\beta\ldots}) &= \langle\Psi_0^{(0)}|[{}^{d}\hat{h}_n^\dagger, \hat{O}^\omega_{\beta\ldots}]|\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}|[{}^{e}\hat{h}_n, \hat{O}^\omega_{\beta\ldots}]|\Psi_0^{(0)}\rangle = -\langle\Psi_0^{(0)}|\hat{O}^\omega_{\beta\ldots}\,{}^{e}\hat{h}_n|\Psi_0^{(0)}\rangle \\
&= -\langle\Psi_0^{(0)}|\hat{O}^\omega_{\beta\ldots}|\Psi_n^{(0)}\rangle
\end{aligned}
$$

<u>3.14</u> First-order correction to the eigenvalues starting from Eq. (3.189):

$$
\mathbf{E}^{(1)}\mathbf{R}_n^{(0)} + \mathbf{E}^{(0)}\mathbf{R}_n^{(1)} = \left(\hbar\omega_n^{(1)}\mathbf{S}^{(0)} + \hbar\omega_n^{(0)}\mathbf{S}^{(1)}\right)\mathbf{R}_n^{(0)} + \hbar\omega_n^{(0)}\mathbf{S}^{(0)}\mathbf{R}_n^{(1)}
$$

and projecting it against the zeroth-order left eigenvector

$$\begin{aligned}\mathbf{L}_n^{(0)}\mathbf{E}^{(1)}\mathbf{R}_n^{(0)} + \mathbf{L}_n^{(0)}\mathbf{E}^{(0)}\mathbf{R}_n^{(1)} = \mathbf{L}_n^{(0)}\left(\hbar\omega_n^{(1)}\mathbf{S}^{(0)} + \hbar\omega_n^{(0)}\mathbf{S}^{(1)}\right)\mathbf{R}_n^{(0)} \\ + \hbar\omega_n^{(0)}\mathbf{L}_n^{(0)}\mathbf{S}^{(0)}\mathbf{R}_n^{(1)}\end{aligned}$$

From Eq. (3.187) and Eq. (3.188) we know

$$\begin{aligned}\mathbf{L}_n^{(0)}\mathbf{E}^{(1)}\mathbf{R}_n^{(0)} &= 0 \\ \mathbf{L}_n^{(0)}\mathbf{S}^{(1)}\mathbf{R}_n^{(0)} &= 0\end{aligned}$$

which leads to

$$\mathbf{L}_n^{(0)}\mathbf{E}^{(0)}\mathbf{R}_n^{(1)} = \hbar\omega_n^{(1)}\mathbf{L}_n^{(0)}\mathbf{S}^{(0)}\mathbf{R}_n^{(0)} + \hbar\omega_n^{(0)}\mathbf{L}_n^{(0)}\mathbf{S}^{(0)}\mathbf{R}_n^{(1)}$$

From Eq. (3.178) and Eq. (3.180) we know

$$\begin{aligned}\mathbf{L}_m\mathbf{S}\mathbf{R}_n &= \delta_{mn} \\ \mathbf{L}_n^{(0)}\mathbf{E}^{(0)} &= \mathbf{L}_n^{(0)}\mathbf{S}^{(0)}\hbar\omega_n^{(0)}\end{aligned}$$

and we can write

$$\begin{aligned}\mathbf{L}_n^{(0)}\mathbf{E}^{(0)}\mathbf{R}_n^{(1)} &= \hbar\omega_n^{(1)} + \hbar\omega_n^{(0)}\mathbf{L}_n^{(0)}\mathbf{S}^{(0)}\mathbf{R}_n^{(1)} \\ \hbar\omega_n^{(1)} &= \mathbf{L}_n^{(0)}\mathbf{E}^{(0)}\mathbf{R}_n^{(1)} - \hbar\omega_n^{(0)}\mathbf{L}_n^{(0)}\mathbf{S}^{(0)}\mathbf{R}_n^{(1)} \\ \hbar\omega_n^{(1)} &= \left(\mathbf{L}_n^{(0)}\mathbf{E}^{(0)} - \hbar\omega_n^{(0)}\mathbf{L}_n^{(0)}\mathbf{S}^{(0)}\right)\mathbf{R}_n^{(1)} \\ \hbar\omega_n^{(1)} &= 0\end{aligned}$$

The second-order correction to the eigenvalues can be derived in a similar way from Eq. (3.190):

$$\begin{aligned}\mathbf{E}^{(2)}\mathbf{R}_n^{(0)} &+ \mathbf{E}^{(1)}\mathbf{R}_n^{(1)} + \mathbf{E}^{(0)}\mathbf{R}_n^{(2)} \\ &= \left(\hbar\omega_n^{(2)}\mathbf{S}^{(0)} + \hbar\omega_n^{(0)}\mathbf{S}^{(2)} + \hbar\omega_n^{(1)}\mathbf{S}^{(1)}\right)\mathbf{R}_n^{(0)} \\ &+ \left(\hbar\omega_n^{(1)}\mathbf{S}^{(0)} + \hbar\omega_n^{(0)}\mathbf{S}^{(1)}\right)\mathbf{R}_n^{(1)} + \hbar\omega_n^{(0)}\mathbf{S}^{(0)}\mathbf{R}_n^{(2)}\end{aligned}$$

Using Eq. (3.175) we can write

$$\begin{aligned}\mathbf{E}^{(2)}\mathbf{R}_n^{(0)} &+ \mathbf{E}^{(1)}\mathbf{R}_n^{(1)} \\ &= \left(\hbar\omega_n^{(2)}\mathbf{S}^{(0)} + \hbar\omega_n^{(0)}\mathbf{S}^{(2)} + \hbar\omega_n^{(1)}\mathbf{S}^{(1)}\right)\mathbf{R}_n^{(0)} \\ &+ \left(\hbar\omega_n^{(1)}\mathbf{S}^{(0)} + \hbar\omega_n^{(0)}\mathbf{S}^{(1)}\right)\mathbf{R}_n^{(1)}\end{aligned}$$

Projecting against the zeroth-order left eigenvector

$$\begin{aligned}
\mathbf{L}_n^{(0)}\mathbf{E}^{(2)}\mathbf{R}_n^{(0)} &+ \mathbf{L}_n^{(0)}\mathbf{E}^{(1)}\mathbf{R}_n^{(1)} \\
&= \mathbf{L}_n^{(0)}\left(\hbar\omega_n^{(2)}\mathbf{S}^{(0)} + \hbar\omega_n^{(0)}\mathbf{S}^{(2)} + \hbar\omega_n^{(1)}\mathbf{S}^{(1)}\right)\mathbf{R}_n^{(0)} \\
&+ \mathbf{L}_n^{(0)}\left(\hbar\omega_n^{(1)}\mathbf{S}^{(0)} + \hbar\omega_n^{(0)}\mathbf{S}^{(1)}\right)\mathbf{R}_n^{(1)} \\
\mathbf{L}_n^{(0)}\mathbf{E}^{(2)}\mathbf{R}_n^{(0)} &+ \mathbf{L}_n^{(0)}\mathbf{E}^{(1)}\mathbf{R}_n^{(1)} \\
&= \hbar\omega_n^{(2)}\mathbf{L}_n^{(0)}\mathbf{S}^{(0)}\mathbf{R}_n^{(0)} + \hbar\omega_n^{(0)}\mathbf{L}_n^{(0)}\mathbf{S}^{(2)}\mathbf{R}_n^{(0)} + \hbar\omega_n^{(1)}\mathbf{L}_n^{(0)}\mathbf{S}^{(1)}\mathbf{R}_n^{(0)} \\
&+ \hbar\omega_n^{(1)}\mathbf{L}_n^{(0)}\mathbf{S}^{(0)}\mathbf{R}_n^{(1)} + \hbar\omega_n^{(0)}\mathbf{L}_n^{(0)}\mathbf{S}^{(1)}\mathbf{R}_n^{(1)} \\
\mathbf{L}_n^{(0)}\mathbf{E}^{(2)}\mathbf{R}_n^{(0)} &+ \mathbf{L}_n^{(0)}\mathbf{E}^{(1)}\mathbf{R}_n^{(1)} \\
&= \hbar\omega_n^{(2)} + \hbar\omega_n^{(0)}\mathbf{L}_n^{(0)}\mathbf{S}^{(2)}\mathbf{R}_n^{(0)} + \hbar\omega_n^{(0)}\mathbf{L}_n^{(0)}\mathbf{S}^{(1)}\mathbf{R}_n^{(1)}
\end{aligned}$$

By rearranging we obtain

$$\hbar\omega_n^{(2)} = \mathbf{L}_n^{(0)}\left(\mathbf{E}^{(2)} - \hbar\omega_n^{(0)}\mathbf{S}^{(2)}\right)\mathbf{R}_n^{(0)} + \mathbf{L}_n^{(0)}\left(\mathbf{E}^{(1)} - \hbar\omega_n^{(0)}\mathbf{S}^{(1)}\right)\mathbf{R}_n^{(1)}$$

Solutions to Chapter 4

4.1 Taking the first partial derivative of $\frac{1}{|\vec{R}-\vec{r}|}$ gives

$$\begin{aligned}
\frac{\partial}{\partial r_\alpha}\frac{1}{\mid \vec{R}-\vec{r}\mid} &= \frac{\partial}{\partial r_\alpha}\left\{\left(\vec{R}-\vec{r}\right)^2\right\}^{-\frac{1}{2}} \\
&= -\frac{1}{2}\left\{\left(\vec{R}-\vec{r}\right)^2\right\}^{-\frac{3}{2}}\frac{\partial}{\partial r_\alpha}\left(\vec{R}-\vec{r}\right)^2 \\
&= -\frac{1}{2}\frac{1}{\mid \vec{R}-\vec{r}\mid^3}\ \frac{\partial}{\partial r_\alpha}\left(\vec{R}^2-2\vec{R}\cdot\vec{r}+\vec{r}^2\right) \\
&= -\frac{1}{2}\frac{1}{\mid \vec{R}-\vec{r}\mid^3}\ \left(-2R_\alpha+2r_\alpha\right) \\
&= \frac{R_\alpha-r_\alpha}{\mid \vec{R}-\vec{r}\mid^3}
\end{aligned}$$

Evaluating this derivative for $\vec{r}=\vec{R}_O$ gives

$$\left(\frac{\partial}{\partial r_\alpha}\frac{1}{\mid \vec{R}-\vec{r}\mid}\right)_{\vec{r}=\vec{R}_O} = \frac{R_\alpha-R_{O,\alpha}}{\mid \vec{R}-\vec{R}_O\mid^3}$$

Taking now the second partial derivative of $\frac{1}{|\vec{R}-\vec{r}|}$ gives

$$\begin{aligned}
\frac{\partial^2}{\partial r_\alpha\partial r_\beta}\frac{1}{\mid \vec{R}-\vec{r}\mid} &= \frac{\partial}{\partial r_\alpha}\frac{R_\beta-r_\beta}{\mid \vec{R}-\vec{r}\mid^3} \\
&= \left(R_\beta-r_\beta\right)\frac{\partial}{\partial r_\alpha}\frac{1}{\mid \vec{R}-\vec{r}\mid^3}+\delta_{\alpha\beta}\left(\frac{\partial}{\partial r_\alpha}\left(R_\beta-r_\beta\right)\right)\frac{1}{\mid \vec{R}-\vec{r}\mid^3} \\
&= \left(R_\beta-r_\beta\right)\frac{\partial}{\partial r_\alpha}\left\{\left(\vec{R}-\vec{r}\right)^2\right\}^{-\frac{3}{2}}+\delta_{\alpha\beta}\left(-1\right)\frac{1}{\mid \vec{R}-\vec{r}\mid^3} \\
&= -\frac{3}{2}\left(R_\beta-r_\beta\right)\left\{\left(\vec{R}-\vec{r}\right)^2\right\}^{-\frac{5}{2}}\frac{\partial}{\partial r_\alpha}\left(\vec{R}-\vec{r}\right)^2-\delta_{\alpha\beta}\frac{1}{\mid \vec{R}-\vec{r}\mid^3} \\
&= -\frac{3}{2}\frac{R_\beta-r_\beta}{\mid \vec{R}-\vec{r}\mid^5}\frac{\partial}{\partial r_\alpha}\left(\vec{R}^2-2\vec{R}\cdot\vec{r}+\vec{r}^2\right)-\delta_{\alpha\beta}\frac{1}{\mid \vec{R}-\vec{r}\mid^3} \\
&= -\frac{3}{2}\frac{R_\beta-r_\beta}{\mid \vec{R}-\vec{r}\mid^5}\left(-2R_\alpha+2r_\alpha\right)-\delta_{\alpha\beta}\frac{1}{\mid \vec{R}-\vec{r}\mid^3}
\end{aligned}$$

and finally

$$\frac{\partial^2}{\partial r_\alpha \partial r_\beta} \frac{1}{|\vec{R} - \vec{r}\,|} = \frac{3\,(R_\beta - r_\beta)\,(R_\alpha - r_\alpha)}{|\vec{R} - \vec{r}\,|^5} - \delta_{\alpha\beta} \frac{1}{|\vec{R} - \vec{r}\,|^3}$$

Evaluating this derivative for $\vec{r} = \vec{R}_O$ gives

$$\left(\frac{\partial^2}{\partial r_\alpha \partial r_\beta} \frac{1}{|\vec{R} - \vec{r}\,|} \right)_{\vec{r} = \vec{R}_O} = \frac{3\,(R_\beta - R_{O,\beta})\,(R_\alpha - R_{O,\alpha})}{|\vec{R} - \vec{R}_O|^5} - \delta_{\alpha\beta} \frac{1}{|\vec{R} - \vec{R}_O|^3}$$

<u>4.2</u> Expanding the definition of the electric dipole moment, Eq. (4.5),

$$\mu_\alpha(\vec{R}_O) = \int_{\vec{r}} (r_\alpha - R_{O,\alpha})\ \rho(\vec{r}\,)\ d\vec{r}$$

as

$$\begin{aligned} \mu_\alpha(\vec{R}_O) &= \int_{\vec{r}} r_\alpha\ \rho(\vec{r}\,)\ d\vec{r} - \int_{\vec{r}} R_{O,\alpha}\ \rho(\vec{r}\,)\ d\vec{r} \\ &= \int_{\vec{r}} r_\alpha\ \rho(\vec{r}\,)\ d\vec{r} - R_{O,\alpha} q \end{aligned}$$

one can see that only for a neutral molecule, $q = 0$, the dipole moment will be independent of the origin $\vec{R}_O$.

Similarly starting from the definition of the traceless quadrupole moment tensor, Eq. (4.8),

$$\Theta_{\alpha\beta}(\vec{R}_O) = \frac{1}{2} \int_{\vec{r}} \left[3(r_\alpha - R_{O,\alpha})\ (r_\beta - R_{O,\beta}) - \delta_{\alpha\beta}\ (\vec{r} - \vec{R}_O)^2 \right]\ \rho(\vec{r}\,)\ d\vec{r}$$

which can be rewritten as

$$\begin{aligned} \Theta_{\alpha\beta}(\vec{R}_O) = & \frac{1}{2} \int_{\vec{r}} \left[3 r_\alpha r_\beta - \delta_{\alpha\beta}\ \vec{r}^{\,2} \right]\ \rho(\vec{r}\,)\ d\vec{r} \\ & - \frac{1}{2} \int_{\vec{r}} \left[3 r_\alpha R_{O,\beta} + 3 R_{O,\alpha} r_\beta - 2\delta_{\alpha\beta}\ (\vec{r} \cdot \vec{R}_O) \right]\ \rho(\vec{r}\,)\ d\vec{r} \\ & + \frac{1}{2} \int_{\vec{r}} \left[3 R_{O,\alpha} R_{O,\beta} - \delta_{\alpha\beta}\ \vec{R}_O^2 \right]\ \rho(\vec{r}\,)\ d\vec{r} \end{aligned}$$

or

$$\begin{aligned} \Theta_{\alpha\beta}(\vec{R}_O) = & \Theta_{\alpha\beta}(\vec{O}) - \frac{3}{2} \mu_\alpha(\vec{O}) R_{O,\beta} - \frac{3}{2} R_{O,\alpha} \mu_\beta(\vec{O}) - \delta_{\alpha\beta} \vec{R}_O \cdot \vec{\mu}(\vec{O}) \\ & + \frac{3}{2} R_{O,\alpha} R_{O,\beta}\ q - \frac{1}{2} \delta_{\alpha\beta}\ \vec{R}_O^2\ q \end{aligned}$$

one can see the quadrupole moment tensor is only independent of the origin $\vec{R}_O$ for a neutral, $q = 0$, and unpolar, $\vec{\mu} = 0$, molecule.

<u>4.3</u> The Taylor expansion of the electric potential, Eq. (4.15), is

$$\phi^{\mathcal{E}}(\vec{r}) = \phi^{\mathcal{E}}(\vec{R}_O) + \sum_{\alpha} (r_\alpha - R_{O,\alpha}) \frac{\partial \phi^{\mathcal{E}}(\vec{r})}{\partial r_\alpha} |_{\vec{r}=\vec{R}_O}$$
$$+ \frac{1}{2} \sum_{\alpha\beta} (r_\alpha - R_{O,\alpha}) (r_\beta - R_{O,\beta}) \frac{\partial^2 \phi^{\mathcal{E}}(\vec{r})}{\partial r_\alpha \partial r_\beta} |_{\vec{r}=\vec{R}_O}$$

where the term depending on the second order electric moment reads

$$\frac{1}{2} \sum_{\alpha\beta} (-r_\alpha - R_{O,\alpha}) (r_\beta - R_{O,\beta}) \frac{\partial^2 \phi^{\mathcal{E}}(\vec{r})}{\partial r_\alpha \partial r_\beta} |_{\vec{r}=\vec{R}_O} = \frac{1}{2} \sum_{\alpha\beta} Q_{\alpha\beta}(\vec{R}_O) \mathcal{E}_{\alpha\beta}(\vec{R}_O)$$

Adding a constant C to the diagonal elements $Q_{\alpha\beta}$ gives

$$\frac{1}{2} \Big[(Q_{xx}(\vec{R}_O) + C)\mathcal{E}_{xx}(\vec{R}_O) + (Q_{yy}(\vec{R}_O) + C)\mathcal{E}_{yy}(\vec{R}_O) + (Q_{zz}(\vec{R}_O) + C)\mathcal{E}_{zz}(\vec{R}_O) \Big]$$
$$= \frac{1}{2} \Big[Q_{xx}(\vec{R}_O)\mathcal{E}_{xx}(\vec{R}_O) + Q_{yy}(\vec{R}_O)\mathcal{E}_{yy}(\vec{R}_O) + Q_{zz}(\vec{R}_O)\mathcal{E}_{zz}(\vec{R}_O) \Big]$$
$$+ \frac{1}{2} C \Big[\mathcal{E}_{xx}(\vec{R}_O) + \mathcal{E}_{yy}(\vec{R}_O) + \mathcal{E}_{zz}(\vec{R}_O) \Big]$$

Collecting the terms including the constant C we obtain

$$\frac{1}{2} \Big[Q_{xx}(\vec{R}_O)\mathcal{E}_{xx}(\vec{R}_O) + Q_{yy}(\vec{R}_O)\mathcal{E}_{yy}(\vec{R}_O) + Q_{zz}(\vec{R}_O)\mathcal{E}_{zz}(\vec{R}_O) \Big]$$
$$+ \frac{1}{2} C \Big[\mathcal{E}_{xx}(\vec{R}_O) + \mathcal{E}_{yy}(\vec{R}_O) + \mathcal{E}_{zz}(\vec{R}_O) \Big]$$
$$= \frac{1}{2} \Big[Q_{xx}(\vec{R}_O)\mathcal{E}_{xx}(\vec{R}_O) + Q_{yy}(\vec{R}_O)\mathcal{E}_{yy}(\vec{R}_O) + Q_{zz}(\vec{R}_O)\mathcal{E}_{zz}(\vec{R}_O) \Big]$$
$$+ \frac{1}{2} C \left[\frac{\partial^2 \phi^{\mathcal{E}}}{\partial x \partial x} + \frac{\partial^2 \phi^{\mathcal{E}}}{\partial y \partial y} + \frac{\partial^2 \phi^{\mathcal{E}}}{\partial z \partial z} \right]$$
$$= \frac{1}{2} \Big[Q_{xx}(\vec{R}_O)\mathcal{E}_{xx}(\vec{R}_O) + Q_{yy}(\vec{R}_O)\mathcal{E}_{yy}(\vec{R}_O) + Q_{zz}(\vec{R}_O)\mathcal{E}_{zz}(\vec{R}_O) \Big]$$
$$+ \frac{1}{2} C \left[\frac{\partial^2}{\partial x \partial x} + \frac{\partial^2}{\partial y \partial y} + \frac{\partial^2}{\partial z \partial z} \right] \phi^{\mathcal{E}}$$
$$= \frac{1}{2} \Big[Q_{xx}(\vec{R}_O)\mathcal{E}_{xx}(\vec{R}_O) + Q_{yy}(\vec{R}_O)\mathcal{E}_{yy}(\vec{R}_O) + Q_{zz}(\vec{R}_O)\mathcal{E}_{zz}(\vec{R}_O) \Big]$$
$$+ \frac{1}{2} C \vec{\nabla}^2 \phi^{\mathcal{E}}$$

Using now Laplace's equation

$$\nabla^2 \phi^{\mathcal{E}}(\vec{R}_O) = 0$$

we finally obtain for this term

$$= \frac{1}{2}\left[Q_{xx}(\vec{R}_O)\mathcal{E}_{xx}(\vec{R}_O) + Q_{yy}(\vec{R}_O)\mathcal{E}_{yy}(\vec{R}_O) + Q_{zz}(\vec{R}_O)\mathcal{E}_{zz}(\vec{R}_O)\right]$$
$$= \frac{1}{2}\sum_\alpha \left[Q_{\alpha\alpha}(\vec{R}_O)\mathcal{E}_{\alpha\alpha}(\vec{R}_O)\right]$$

This terms is thus unchanged by adding a constant C to the diagonal elements of the second electric moment tensor $\mathbf{Q}$, Eq. (4.6).

4.4 In Eq. (4.18), the traceless quadrupole moment tensor, Eq. (4.8), is used instead of the second-order electric moment, Eq. (4.6),

$$Q_{\alpha\beta}(\vec{R}_O) = \int_{\vec{r}} (r_\alpha - R_{O,\alpha})(r_\beta - R_{O,\beta})\rho(\vec{r})d\vec{r}$$

in the Taylor expansion of the electric potential. But the quadrupole moment tensor can be rewritten as

$$\Theta_{\alpha\beta}(\vec{R}_O) = \frac{1}{2}\int_{\vec{r}} \left[3(r_\alpha - R_{O,\alpha})(r_\beta - R_{O,\beta}) - \delta_{\alpha\beta}(\vec{r} - \vec{R}_O)^2\right]\rho(\vec{r})d\vec{r}$$
$$= \frac{3}{2}\int_{\vec{r}} (r_\alpha - R_{O,\alpha})(r_\beta - R_{O,\beta})\rho(\vec{r})d\vec{r} - \frac{1}{2}\int_{\vec{r}} \delta_{\alpha\beta}(\vec{r} - \vec{R}_O)^2\rho(\vec{r})d\vec{r}$$
$$= \frac{3}{2}Q_{\alpha\beta} - \frac{1}{2}\int_{\vec{r}} \delta_{\alpha\beta}(\vec{r} - \vec{R}_O)^2\rho(\vec{r})d\vec{r}$$
$$= \frac{3}{2}Q_{\alpha\beta} - \frac{1}{2}\delta_{\alpha\beta}\sum_\gamma Q_{\gamma\gamma}$$

which implies that it is essentially the second electric moment tensor with a constant added to the diagonal elements, which leaves the electric potential unchanged, as shown in Exercise 4.3.

4.5 Verification of Eq. (4.62) with an electric field $(\mathcal{E}_x, \mathcal{E}_y, 0)$ and the dipole moment only expanded in the polarizability. The line integral

$$\sum_\alpha \int_{(0,0,0)}^{(\mathcal{E}_x,\mathcal{E}_y,0)} \left(\mu_\alpha + \sum_\beta \alpha_{\alpha\beta}\mathcal{E}'_\beta\right) d\mathcal{E}'_\alpha$$

is independent of the path and we can therefore integrate in two steps: one from $(0,0,0)$ to $(\mathcal{E}_x,0,0)$ and the second from $(\mathcal{E}_x,0,0)$ to $(\mathcal{E}_x,\mathcal{E}_y,0)$

$$\sum_\alpha \int_{(0,0,0)}^{(\mathcal{E}_x,\mathcal{E}_y,0)} \left(\mu_\alpha + \sum_\beta \alpha_{\alpha\beta}\mathcal{E}'_\beta\right) d\mathcal{E}'_\alpha$$
$$= \sum_\alpha \int_{(0,0,0)}^{(\mathcal{E}_x,0,0)} \left(\mu_\alpha + \sum_\beta \alpha_{\alpha\beta}\mathcal{E}'_\beta\right) d\mathcal{E}'_\alpha + \sum_\alpha \int_{(\mathcal{E}_x,0,0)}^{(\mathcal{E}_x,\mathcal{E}_y,0)} \left(\mu_\alpha + \sum_\beta \alpha_{\alpha\beta}\mathcal{E}'_\beta\right) d\mathcal{E}'_\alpha$$

or

$$= \int_{(0,0,0)}^{(\mathcal{E}_x,0,0)} (\mu_x + \alpha_{xx}\mathcal{E}'_x)\, d\mathcal{E}'_x + \int_{(\mathcal{E}_x,0,0)}^{(\mathcal{E}_x,\mathcal{E}_y,0)} \left(\mu_y + \alpha_{yx}\mathcal{E}_x + \alpha_{yy}\mathcal{E}'_y\right) d\mathcal{E}'_y$$

Integration gives then

$$\sum_\alpha \int_{(0,0,0)}^{(\mathcal{E}_x,\mathcal{E}_y,0)} \left(\mu_\alpha + \sum_\beta \alpha_{\alpha\beta}\mathcal{E}'_\beta\right) d\mathcal{E}'_\alpha$$

$$= \mu_x\mathcal{E}_x + \frac{1}{2}\alpha_{xx}\mathcal{E}_x^2 + \mu_y\mathcal{E}_y + \alpha_{xy}\mathcal{E}_x\mathcal{E}_y + \frac{1}{2}\alpha_{yy}\mathcal{E}_y^2$$

$$= \sum_{\alpha=x,y} \mu_\alpha\mathcal{E}_\alpha + \frac{1}{2}\left(\alpha_{xy}\mathcal{E}_x\mathcal{E}_y + \alpha_{yx}\mathcal{E}_x\mathcal{E}_y\right) + \frac{1}{2}\alpha_{xx}\mathcal{E}_x^2 + \frac{1}{2}\alpha_{yy}\mathcal{E}_y^2$$

Finally using

$$\alpha_{xy} = \alpha_{yx}$$

one obtains

$$\sum_\alpha \int_{(0,0,0)}^{(\mathcal{E}_x,\mathcal{E}_y,0)} \left(\mu_\alpha + \sum_\beta \alpha_{\alpha\beta}\mathcal{E}'_\beta\right) d\mathcal{E}'_\alpha = \sum_{\alpha=x,y} \left(\mu_\alpha\mathcal{E}_\alpha + \sum_{\beta=x,y} \frac{1}{2}\alpha_{\alpha\beta}\mathcal{E}_\alpha\mathcal{E}_\beta\right)$$

4.6 In Eq. (4.14) the electric field gradient tensor is defined as

$$\mathcal{E}_{\alpha\beta}(\vec{R}) = -\frac{\partial^2 \phi^\rho(\vec{r})}{\partial R_\alpha \partial R_\beta}$$

Inserting the definition of the electrostatic potential, Eq. (4.1),

$$\phi^\rho(\vec{R}) = \frac{1}{4\pi\epsilon_0} \int_{\vec{r}} \frac{\rho(\vec{r})}{|\vec{R}-\vec{r}|} d\vec{r}$$

one obtains

$$\mathcal{E}_{\alpha\beta}(\vec{R}) = -\frac{1}{4\pi\epsilon_0} \frac{\partial^2}{\partial R_\alpha \partial R_\beta} \left(\int_{\vec{r}} \frac{\rho(\vec{r})}{|\vec{R}-\vec{r}|} d\vec{r}\right)$$

$$= -\frac{1}{4\pi\epsilon_0} \int_{\vec{r}} \rho(\vec{r}) \frac{\partial^2}{\partial R_\alpha \partial R_\beta} \frac{1}{|\vec{R}-\vec{r}|}$$

Using the result from Exercise 4.1, but differentiating now with respect to $\vec{R}$ and not $\vec{r}$, we can write:

$$\mathcal{E}_{\alpha\beta}(\vec{R}) = -\frac{1}{4\pi\epsilon_0} \int_{\vec{r}} \rho(\vec{r}) \left[\frac{\delta_{\alpha\beta}}{|\vec{R}-\vec{r}|^3} - 3\frac{(R_\alpha - r_\alpha)(R_\beta - r_\beta)}{|\vec{R}-\vec{r}|^5}\right] d\vec{r}$$

Solutions to Chapter 5

5.1 In the exercise it was given that

$$\oint f(\vec{r})\vec{j}(\vec{r}) \cdot d\vec{S}' = 0$$

for a bounding surface $\vec{S}'$ which completely encloses the current distribution $\vec{j}(\vec{r})$. Using the divergence theorem one can rewrite it as

$$\oint f(\vec{r})\vec{j}(\vec{r}) \cdot d\vec{S}' = \int_{\vec{r}} \vec{\nabla} \cdot \left[f(\vec{r})\vec{j}(\vec{r})\right] d\vec{r} = 0$$

where $d\vec{r}$ is the volume element inside of $\vec{S}'$. Using the general rule of vector calculus

$$\vec{\nabla} \cdot [g(\vec{r})\vec{a}(\vec{r})] = \vec{a}(\vec{r}) \cdot \vec{\nabla} g(\vec{r}) + g(\vec{r})\vec{\nabla} \cdot \vec{a}(\vec{r})$$

we obtain for the r.h.s.

$$\int_{\vec{r}} \vec{\nabla} \cdot \left[f(\vec{r})\vec{j}(\vec{r})\right] d\vec{r} = \int_{\vec{r}} \left[\vec{j}(\vec{r}) \cdot \vec{\nabla} f(\vec{r}) + f(\vec{r})\vec{\nabla} \cdot \vec{j}(\vec{r})\right] d\vec{r} = 0$$

And since

$$\vec{\nabla} \cdot \vec{j} = 0$$

for a steady current, we get the result

$$\oint f(\vec{r})\vec{j}(\vec{r}) \cdot d\vec{S}' = \int_{\vec{r}} \left[\vec{\nabla} f(\vec{r})\right] \cdot \vec{j}(\vec{r}) d\vec{r} = 0$$

which is what we wanted to show.

5.2 From Eq. (5.5) we have

$$\int_{\vec{r}} \left[\vec{\nabla} f(\vec{r})\right] \cdot \vec{j}(\vec{r}) d\vec{r} = 0$$

Choosing the arbitrary function as

$$f(\vec{r}) = r_\alpha$$

we obtain

$$\int_{\vec{r}} \left[\vec{\nabla} r_\alpha\right] \cdot \vec{j}(\vec{r}) d\vec{r} = 0$$

and thus

$$\int_{\vec{r}} j_\alpha(\vec{r}) d\vec{r} = 0$$

If we choose instead

$$f(\vec{r}) = (r_\alpha - R_{GO,\alpha})(r_\beta - R_{GO,\beta})$$

we get

$$\int_{\vec{r}} \left[\vec{\nabla} \left\{ (r_\alpha - R_{GO,\alpha})(r_\beta - R_{GO,\beta}) \right\}) \right] \cdot \vec{j}(\vec{r}) d\vec{r} = 0$$

or

$$\int_{\vec{r}} \left[\vec{e}_\alpha (r_\beta - R_{GO,\beta}) + \vec{e}_\beta (r_\alpha - R_{GO,\alpha}) \right] \cdot \vec{j}(\vec{r}) d\vec{r} = 0$$

where $\vec{e}_\alpha$ and $\vec{e}_\beta$ are unit vectors in α or β direction. This yields then the expression

$$\int_{\vec{r}} \left[(r_\beta - R_{GO,\beta}) j_\alpha(\vec{r}) + (r_\alpha - R_{GO,\alpha}) j_\beta(\vec{r}) \right] d\vec{r} = 0$$

which is what we wanted to show.

5.3 The definition of the magnetic dipole moment, Eq. (5.10), can be expanded as

$$\begin{aligned} \vec{m} &= \frac{1}{2} \int_{\vec{r}} (\vec{r} - \vec{R}_{GO}) \times \vec{j}(\vec{r}) d\vec{r} \\ &= \frac{1}{2} \int_{\vec{r}} \vec{r} \times \vec{j}(\vec{r}) d\vec{r} - \frac{1}{2} \int_{\vec{r}} \vec{R}_{GO} \times \vec{j}(\vec{r}) d\vec{r} \\ &= \frac{1}{2} \int_{\vec{r}} \vec{r} \times \vec{j}(\vec{r}) d\vec{r} - \frac{1}{2} \vec{R}_{GO} \times \int_{\vec{r}} \vec{j}(\vec{r}) d\vec{r} \end{aligned}$$

Using

$$\int_{\vec{r}} j_\alpha(\vec{r}) d\vec{r} = 0$$

we get

$$\vec{m} = \frac{1}{2} \int_{\vec{r}} \vec{r} \times \vec{j}(\vec{r}) d\vec{r}$$

which shows that the magnetic dipole moment is independent of the gauge origin $\vec{R}_{GO}$.

5.4 The first-order molecular Hamiltonian reads for magnetic perturbations

$$\hat{H}^{(1)} = \sum_i^N \hat{h}^{(1)}(i)$$

with

$$\hat{h}^{(1)}(i) = \frac{e}{m_e} \hat{\vec{A}}(\vec{r}_i) \cdot \hat{\vec{p}}_i + \frac{g_e e}{2m_e} \hat{\vec{s}}_i \cdot \left[\hat{\vec{\nabla}} \times \hat{\vec{A}}(\vec{r}_i) \right]$$

For the vector potential of a homogenous magnetic induction, Eq. (5.19),

$$\hat{\vec{A}}^{\mathcal{B}}(\vec{r}_i) = \frac{1}{2} \vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO})$$

the operator becomes

$$\hat{h}^{(1)}(i) = \frac{e}{m_e} \frac{1}{2} \left[\vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO}) \right] \cdot \hat{\vec{p}}_i + \frac{g_e e}{2m_e} \hat{\vec{s}}_i \cdot \left[\hat{\vec{\nabla}} \times \hat{\vec{A}}(\vec{r}_i) \right]$$

Using then the general rule of calculus

$$(\vec{A} \times \vec{B}) \cdot \vec{C} = (\vec{B} \times \vec{C}) \cdot \vec{A}$$

and the fact that

$$\hat{\vec{B}} = \hat{\vec{\nabla}} \times \hat{\vec{A}}(\vec{r}_i)$$

we get

$$\hat{h}^{(1)}(i) = \frac{e}{2m_e} \left[(\vec{r}_i - \vec{R}_{GO}) \times \hat{\vec{p}}_i \right] \cdot \vec{\mathcal{B}} + \frac{g_e e}{2m_e} \hat{\vec{s}}_i \cdot \hat{\vec{B}}$$

If we define

$$\frac{e}{2m_e} \left[(\vec{r}_i - \vec{R}_{GO}) \times \hat{\vec{p}}_i \right] \cdot \vec{\mathcal{B}} = -\sum_\alpha \mathcal{B}_\alpha \hat{o}^{l\mathcal{B}}_{i,\alpha}(\vec{R}_{GO})$$

where

$$\hat{o}^{l\mathcal{B}}_{i,\alpha}(\vec{R}_{GO}) = -\frac{e}{2m_e} \left[(\vec{r}_i - \vec{R}_{GO}) \times \hat{\vec{p}}_i \right]_\alpha$$

and similarly

$$\frac{g_e e}{2m_e} \hat{\vec{s}}_i \cdot \hat{\vec{B}} = -\sum_\alpha \mathcal{B}_\alpha \hat{o}^{s\mathcal{B}}_{i,\alpha}$$

where

$$\hat{o}^{s\mathcal{B}}_{i,\alpha} = -\frac{g_e e}{2m_e} \hat{\vec{s}}_{i,\alpha}$$

we can write the first-order perturbation Hamiltonian operator as

$$\hat{H}^{(1)} = \sum_i^N \hat{h}^{(1)}(i) + \hat{H}^{(1)}_{nuc} = -\sum_i^N \sum_\alpha \mathcal{B}_\alpha \left[\hat{o}^{s\mathcal{B}}_{i,\alpha} + \hat{o}^{l\mathcal{B}}_{i,\alpha}(\vec{R}_{GO}) \right] = -\sum_\alpha \mathcal{B}_\alpha \left[\hat{O}^{s\mathcal{B}}_\alpha + \hat{O}^{l\mathcal{B}}_\alpha(\vec{R}_{GO}) \right]$$

where

$$\hat{O}^{s\mathcal{B}}_\alpha = \sum_i^N \hat{o}^{s\mathcal{B}}_{i,\alpha}$$

$$\hat{O}^{l\mathcal{B}}_\alpha(\vec{R}_{GO}) = \sum_i^N \hat{o}^{l\mathcal{B}}_{i,\alpha}(\vec{R}_{GO})$$

which is what we wanted to show.

5.5 The second-order molecular Hamiltonian reads for magnetic perturbations

$$\hat{H}^{(2)} = \sum_i^N \hat{h}^{(2)}(i)$$

with

$$\hat{h}^{(2)}(i) = \frac{e^2}{2m_e} \hat{\vec{A}}^2(\vec{r}_i)$$

Inserting the vector potential, Eq. (5.19), this reads

$$
\begin{aligned}
\hat{h}^{(2)}(i) &= \frac{e^2}{2m_e}\left[\frac{1}{2}\vec{\mathcal{B}}\times(\vec{r}_i-\vec{R}_{GO})\right]^2 \\
&= \frac{e^2}{8m_e}\left[\vec{\mathcal{B}}\times(\vec{r}_i-\vec{R}_{GO})\right]\left[\vec{\mathcal{B}}\times(\vec{r}_i-\vec{R}_{GO})\right]
\end{aligned}
$$

If we use the relation

$$
(\vec{A}\times\vec{B})(\vec{C}\times\vec{D}) = \vec{A}\,(\vec{D}\cdot\vec{B}\,\boldsymbol{I}_3 - \vec{D}\vec{B}^T)\,\vec{C}
$$

the second-order operator becomes

$$
\begin{aligned}
\hat{h}^{(2)}(i) &= \frac{e^2}{8m_e}\vec{\mathcal{B}}\left[(\vec{r}_i-\vec{R}_{GO})\cdot(\vec{r}_i-\vec{R}_{GO})\,\boldsymbol{I}_3 - (\vec{r}_i-\vec{R}_{GO})(\vec{r}_i-\vec{R}_{GO})^T\right]\vec{\mathcal{B}} \\
&= \frac{e^2}{8m_e}\sum_{\alpha\beta}\mathcal{B}_\alpha\left[(\vec{r}_i-\vec{R}_{GO})^2\cdot\delta_{\alpha\beta} - (\vec{r}_{i,\alpha}-\vec{R}_{GO,\alpha})(\vec{r}_{i,\beta}-\vec{R}_{GO,\beta})\right]\mathcal{B}_\beta \\
&= \sum_{\alpha\beta}\hat{o}^{\mathcal{BB}}_{i,\alpha\beta}(\vec{R}_{GO})\mathcal{B}_\alpha\mathcal{B}_\beta
\end{aligned}
$$

and the second order perturbation Hamiltonian is

$$
\begin{aligned}
\hat{H}^{(2)} &= \sum_i^N \hat{h}^{(2)}(i) = \sum_i^N \frac{e^2}{2m_e}\hat{\vec{A}}^2(\vec{r}_i) \\
&= \frac{e^2}{8m_e}\sum_i^N\sum_{\alpha\beta}\mathcal{B}_\alpha\mathcal{B}_\beta\left((r_{i,\alpha}-R_{GO,\alpha})^2\delta_{\alpha\beta} - (r_{i,\alpha}-R_{GO,\alpha})(r_{i,\beta}-R_{GO,\beta})\right) \\
&= \sum_{\alpha\beta}\hat{O}^{\mathcal{BB}}_{\alpha\beta}(\vec{R}_{GO})\mathcal{B}_\alpha\mathcal{B}_\beta
\end{aligned}
$$

where

$$
\begin{aligned}
\hat{O}^{\mathcal{BB}}_{\alpha\beta}(\vec{R}_{GO}) &= \sum_i^N \hat{o}^{\mathcal{BB}}_{i,\alpha\beta}(\vec{R}_{GO}) \\
&= \frac{e^2}{8m_e}\sum_i^N\left((r_{i,\alpha}-R_{GO,\alpha})^2\delta_{\alpha\beta} - (r_{i,\alpha}-R_{GO,\alpha})(r_{i,\beta}-R_{GO,\beta})\right)
\end{aligned}
$$

This is what we wanted to show.

5.6 Inserting the vector potential from Eq. (5.2)

$$
\vec{A}^j(\vec{R}) = \frac{\mu_0}{4\pi}\int_{\vec{r}}\frac{\vec{j}(\vec{r})}{|\vec{R}-\vec{r}|}d\vec{r}
$$

into Eq. (5.19)

$$
\vec{\mathcal{B}}^j(\vec{R}) = \vec{\nabla}\times\vec{A}^j(\vec{R})
$$

we get

$$\vec{\mathcal{B}}^j(\vec{R}) = \vec{\nabla} \times \frac{\mu_0}{4\pi} \int_{\vec{r}} \frac{\vec{j}(\vec{r})}{|\vec{R}-\vec{r}|} d\vec{r} = \frac{\mu_0}{4\pi} \int_{\vec{r}} \vec{\nabla} \times \frac{\vec{j}(\vec{r})}{|\vec{R}-\vec{r}|} d\vec{r}$$

If we look now at the x-component, we obtain

$$\begin{aligned}
\mathcal{B}_x^j(\vec{R}) &= \frac{\mu_0}{4\pi} \int_{\vec{r}} \left[\vec{\nabla} \times \frac{j(\vec{r})}{|\vec{R}-\vec{r}|} \right]_x d\vec{r} \\
&= \frac{\mu_0}{4\pi} \int_{\vec{r}} \left[\frac{\partial}{\partial R_y} \frac{j_z(\vec{r})}{|\vec{R}-\vec{r}|} - \frac{\partial}{\partial R_z} \frac{j_y(\vec{r})}{|\vec{R}-\vec{r}|} \right] d\vec{r} \\
&= \frac{\mu_0}{4\pi} \int_{\vec{r}} \left[j_z(\vec{r}) \frac{\partial}{\partial R_y} \frac{1}{|\vec{R}-\vec{r}|} - j_y(\vec{r}) \frac{\partial}{\partial R_z} \frac{1}{|\vec{R}-\vec{r}|} \right] d\vec{r} \\
&= \frac{\mu_0}{4\pi} \int_{\vec{r}} \left[-j_z(\vec{r}) \frac{(R_y - r_y)}{|\vec{R}-\vec{r}|^3} + j_y(\vec{r}) \frac{(R_z - r_z)}{|\vec{R}-\vec{r}|^3} \right] d\vec{r} \\
&= -\frac{\mu_0}{4\pi} \int_{\vec{r}} \left[\frac{(R_y - r_y)}{|\vec{R}-\vec{r}|^3} j_z(\vec{r}) - \frac{(R_z - r_z)}{|\vec{R}-\vec{r}|^3} j_y(\vec{r}) \right] d\vec{r} \\
&= -\frac{\mu_0}{4\pi} \int_{\vec{r}} \left[\frac{(\vec{R}-\vec{r})}{|\vec{R}-\vec{r}|^3} \times \vec{j}(\vec{r}) \right]_x d\vec{r}
\end{aligned}$$

and analogously for the other components. Using this the permanent molecular magnetic induction can be written as

$$\begin{aligned}
\vec{\mathcal{B}}^j(\vec{R}) &= -\frac{\mu_0}{4\pi} \int_{\vec{r}} \frac{(\vec{R}-\vec{r}) \times \vec{j}(\vec{r})}{|\vec{R}-\vec{r}|^3} d\vec{r} \\
&= -\frac{\mu_0}{4\pi} \int_{\vec{r}} \rho(\vec{r}) \frac{(\vec{R}-\vec{r}) \times \vec{v}(\vec{r})}{|\vec{R}-\vec{r}|^3} d\vec{r}
\end{aligned}$$

5.7 The first-order molecular Hamiltonian reads again

$$\begin{aligned}
\hat{H}^{(1)} &= \sum_i^N \hat{h}^{(1)}(i) \\
\hat{h}^{(1)}(i) &= \frac{e}{m_e} \hat{\vec{A}}(\vec{r}_i) \cdot \hat{\vec{p}}_i + \frac{g_e e}{2m_e} \hat{\vec{s}}_i \cdot \left[\hat{\vec{\nabla}} \times \hat{\vec{A}}(\vec{r}_i) \right]
\end{aligned}$$

but now the vector potential is the potential of a nuclear magnetic dipole

$$\hat{\vec{A}}^K(\vec{r}_i) = \frac{\mu_0}{4\pi} \vec{m}^K \times \frac{\left(\vec{r}_i - \vec{R}_K \right)}{|\vec{r}_i - \vec{R}_K|^3}$$

For the first term of $\hat{h}^{(1)}(i)$ we get

$$\frac{e}{m_e}\hat{\vec{A}}(\vec{r}_i)\cdot\hat{\vec{p}}_i = \frac{e}{m_e}\left[\frac{\mu_0}{4\pi}\vec{m}^K \times \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right]\cdot\hat{\vec{p}}_i$$

$$= \frac{e}{m_e}\frac{\mu_0}{4\pi}\left[\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\times\hat{\vec{p}}_i\right]\cdot\vec{m}^K$$

$$= \frac{e}{m_e}\frac{\mu_0}{4\pi}\frac{\hat{\vec{l}}_i(\vec{R}_K)}{|\vec{r}_i - \vec{R}_K|^3}\cdot\vec{m}^K$$

For the second term of $\hat{h}^{(1)}(i)$ we get

$$\frac{g_e e}{2m_e}\hat{\vec{s}}_i\cdot\left[\hat{\vec{\nabla}}\times\hat{\vec{A}}(\vec{r}_i)\right] = \frac{g_e e}{2m_e}\hat{\vec{s}}_i\cdot\left\{\hat{\vec{\nabla}}\times\left[\frac{\mu_0}{4\pi}\vec{m}^K\times\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right]\right\}$$

$$= \frac{g_e e}{2m_e}\frac{\mu_0}{4\pi}\hat{\vec{s}}_i\cdot\left\{\hat{\vec{\nabla}}\times\left[\vec{m}^K\times\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right]\right\}$$

Then we use the general rule of vector calculus

$$\vec{\nabla}\times\left(\vec{A}\times\vec{B}\right) = \vec{A}\left(\vec{\nabla}\cdot\vec{B}\right) - \vec{B}\left(\vec{\nabla}\cdot\vec{A}\right) + \left(\vec{B}\cdot\vec{\nabla}\right)\vec{A} - \left(\vec{A}\cdot\vec{\nabla}\right)\vec{B}$$

However, in our case the second and the third terms on the right hand side are equal to zero, as the gradient of the nuclear magnetic moment with respect to electronic coordinates is zero. We thus get

$$\frac{g_e e}{2m_e}\hat{\vec{s}}_i\cdot\left[\hat{\vec{\nabla}}\times\hat{\vec{A}}(\vec{r}_i)\right] = \frac{g_e e}{2m_e}\frac{\mu_0}{4\pi}\hat{\vec{s}}_i\cdot\left\{\vec{m}^K\left[\nabla\cdot\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right] - \left(\vec{m}^K\cdot\nabla\right)\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right\}$$

Let us look at the two terms in the curly bracket individually. Using the results of exercise 4.1, i.e.

$$\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3} = -\vec{\nabla}\frac{1}{|\vec{r}_i - \vec{R}_K|}$$

we get for the first term

$$\vec{m}^K\left[\vec{\nabla}\cdot\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right] = -\vec{m}^K\left(\vec{\nabla}^2\frac{1}{|\vec{r}_i - \vec{R}_K|}\right)$$

$$= \vec{m}^K 4\pi\delta(\vec{r}_i - \vec{R}_K)$$

The second term we can rewrite as

$$\left(\vec{m}^K \cdot \vec{\nabla}\right) \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3} = \left(\sum_\alpha m_\alpha^K \frac{\partial}{\partial r_{i,\alpha}}\right) \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}$$

If we now look at the β component, we obtain

$$\begin{aligned}
\left(\sum_\alpha m_\alpha^K \frac{\partial}{\partial r_{i,\alpha}}\right) \left[\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right]_\beta &= \sum_\alpha m_\alpha^K \frac{\partial}{\partial r_{i,\alpha}} \frac{(r_{i,\beta} - R_{K,\beta})}{|r_i - R_K|^3} \\
&= \sum_\alpha m_\alpha^K \left(r_{i,\beta} - R_{K,\beta}\right) \frac{\partial}{\partial r_{i,\alpha}} \frac{1}{|\vec{r}_i - \vec{R}_K|^3} \\
&+ \sum_\alpha \frac{m_\alpha^K}{|\vec{r}_i - \vec{R}_K|^3} \frac{\partial}{\partial r_{i,\alpha}} \left(r_{i,\beta} - R_{K,\beta}\right)
\end{aligned}$$

The second term in the last expression is only different from zero when $\alpha = \beta$, and we thus get

$$\begin{aligned}
\left(\sum_\alpha m_\alpha^K \frac{\partial}{\partial r_{i,\alpha}}\right) \left[\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right]_\beta &= \sum_\alpha m_\alpha^K \left(r_{i,\beta} - R_{K,\beta}\right) (-3) \frac{(r_{i,\alpha} - R_{K,\alpha})}{|\vec{r}_i - \vec{R}_K|^5} \\
&+ \frac{m_\beta^K}{|\vec{r}_i - \vec{R}_K|^3} \\
&= \frac{m_\beta^K}{|\vec{r}_i - \vec{R}_K|^3} - 3 \frac{\vec{m}^K \cdot \left(\vec{r}_i - \vec{R}_K\right) (r_{i,\beta} - R_{K,\beta})}{|\vec{r}_i - \vec{R}_K|^5}
\end{aligned}$$

and analogously for the other components. For the whole vector we obtain then

$$\left(\vec{m}^K \cdot \vec{\nabla}\right) \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3} = \frac{\vec{m}^K}{|\vec{r}_i - \vec{R}_K|^3} - 3 \frac{\vec{m}^K \cdot \left(\vec{r}_i - \vec{R}_K\right) \left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^5}$$

However, this derivation is not valid, if $|\vec{r}_i - \vec{R}_K|$ approaches zero, and we have to take care of this special case. For $\vec{r}_i = \vec{R}_K$ only the total symmetric component of the operator can contribute and we have therefore to calculate the isotropic part of the operator, i.e.

$$\left\langle \left(\vec{m}^K \cdot \vec{\nabla}\right) \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3} \right\rangle$$

For that we have to realize that $\vec{m}^K \cdot \vec{\nabla} \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}$ can be considered as the product of the vector $\vec{m}^K$ with the tensor $\vec{\nabla} \frac{\left(\vec{r}_i - \vec{R}_K\right)^T}{|\vec{r}_i - \vec{R}_K|^3}$. Using again that

$$\frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3} = -\vec{\nabla} \frac{1}{|\vec{r}_i - \vec{R}_K|}$$

we have to calculate the isotropic component of it, i.e.

$$\begin{aligned} -\frac{1}{3} \text{Trace} \left\{ \vec{\nabla} \left(\vec{\nabla} \frac{1}{|\vec{r}_i - \vec{R}_K|} \right)^T \right\} &= -\frac{1}{3} \left(\vec{\nabla}_x \vec{\nabla}_x + \vec{\nabla}_y \vec{\nabla}_y + \vec{\nabla}_z \vec{\nabla}_z \right) \frac{1}{|\vec{r}_i - \vec{R}_K|} \\ &= -\frac{1}{3} \vec{\nabla}^2 \frac{1}{|\vec{r}_i - \vec{R}_K|} \end{aligned}$$

Finally using again that $\vec{\nabla}^2 \frac{1}{|\vec{r}_i - \vec{R}_K|} = -4\pi\delta(\vec{r}_i - \vec{R}_K)$ we obtain finally for $\vec{r}_i = \vec{R}_K$ the additional contribution

$$\left\langle \left(\vec{m}^K \cdot \vec{\nabla} \right) \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3} \right\rangle = \frac{1}{3} \vec{m}^K 4\pi\delta(\vec{r}_i - \vec{R}_K)$$

Collecting now all contributions to the second term of $\hat{h}^{(1)}(i)$ we obtain

$$\begin{aligned} \frac{g_e e}{2m_e} \hat{\vec{s}}_i \cdot \left[\hat{\vec{\nabla}} \times \hat{\vec{A}}(\vec{r}_i) \right] &= \frac{g_e e}{2m_e} \frac{\mu_0}{4\pi} \hat{\vec{s}}_i \cdot \left\{ \vec{m}^K 4\pi\delta(\vec{r}_i - \vec{R}_K) - \frac{1}{3} \vec{m}^K \left[4\pi\delta(\vec{r}_i - \vec{R}_K) \right] \right\} \\ &\quad + \frac{g_e e}{2m_e} \frac{\mu_0}{4\pi} \hat{\vec{s}}_i \cdot \left[3 \frac{\vec{m}^K \cdot \left(\vec{r}_i - \vec{R}_K\right) \left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^5} - \frac{\vec{m}^K}{|\vec{r}_i - \vec{R}_K|^3} \right] \\ &= \frac{g_e e \mu_0}{3m_e} \hat{\vec{s}}_i \cdot \vec{m}^K \delta(\vec{r}_i - \vec{R}_K) \\ &\quad + \frac{g_e e}{2m_e} \frac{\mu_0}{4\pi} \vec{m}^K \cdot \left[3 \frac{\hat{\vec{s}}_i \cdot \left(\vec{r}_i - \vec{R}_K\right) \left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^5} - \frac{\hat{\vec{s}}_i}{|\vec{r}_i - \vec{R}_K|^3} \right] \end{aligned}$$

The first-order perturbation Hamiltonian becomes then finally

$$\begin{aligned}
\hat{H}^{(1)} &= \sum_i^N \hat{h}^{(1)}(i) \\
&= \sum_i^N \frac{e}{m_e} \hat{\vec{A}}(\vec{r}_i) \cdot \hat{\vec{p}}_i + \frac{g_e e}{2m_e} \hat{\vec{s}}_i \cdot \left[\hat{\vec{\nabla}} \times \hat{\vec{A}}(\vec{r}_i) \right] \\
&= - \sum_\alpha \left(\hat{O}_\alpha^{lm^K} + \hat{O}_\alpha^{sm^K} \right) m_\alpha^K
\end{aligned}$$

where

$$\begin{aligned}
\hat{O}_\alpha^{lm^K} &= -\frac{e}{m_e} \frac{\mu_0}{4\pi} \sum_i^N \frac{\hat{l}_{i,\alpha}(R_K)}{|\vec{r}_i - \vec{R}_K|^3} \\
\hat{O}_\alpha^{sm^K} &= \hat{O}_{K,\alpha}^{FC} + \hat{O}_{K,\alpha}^{SD} \\
\hat{O}_{K,\alpha}^{FC} &= -\frac{g_e e \mu_0}{3m_e} \sum_i^N \delta(\vec{r}_i - \vec{R}_K) \hat{s}_{i,\alpha} \\
\hat{O}_{K,\alpha}^{SD} &= -\frac{g_e e}{2m_e} \frac{\mu_0}{4\pi} \sum_i^N \left[3 \frac{\hat{\vec{s}}_i \cdot \left(\vec{r}_i - \vec{R}_K \right) (r_{i,\alpha} - R_{K,\alpha})}{|\vec{r}_i - \vec{R}_K|^5} - \frac{\hat{s}_{i,\alpha}}{|\vec{r}_i - \vec{R}_K|^3} \right]
\end{aligned}$$

5.8 The second-order molecular Hamiltonian is given as

$$\hat{H}^{(2)} = \sum_i^N \hat{h}^{(2)}(i)$$

where

$$\hat{h}^{(2)}(i) = \frac{e^2}{2m_e} \hat{\vec{A}}^2(\vec{r}_i)$$

and

$$\hat{\vec{A}}(\vec{r}_i) = \hat{\vec{A}}^{\mathcal{B}}(\vec{r}_i) + \sum_K \hat{\vec{A}}^K(\vec{r}_i) = \frac{1}{2} \vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO}) + \sum_K \frac{\mu_0}{4\pi} \vec{m}^K \times \frac{\left(\vec{r}_i - \vec{R}_K \right)}{|\vec{r}_i - \vec{R}_K|^3}$$

Let us therefore look first at $\hat{\vec{A}}(\vec{r}_i)^2$, where however, the summation over the nuclei in the second term was changed from K to L

$$\hat{\vec{A}}(\vec{r}_i)^2 = \left[\hat{\vec{A}}^{\mathcal{B}}(\vec{r}_i) + \sum_K \hat{\vec{A}}^K(\vec{r}_i) \right] \cdot \left[\hat{\vec{A}}^{\mathcal{B}}(\vec{r}_i) + \sum_L \hat{\vec{A}}^L(\vec{r}_i) \right]$$

or

$$\hat{\vec{A}}(\vec{r}_i)^2 = \left[\frac{1}{2}\vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO})\right]^2 + \left[\sum_K \frac{\mu_0}{4\pi}\vec{m}^K \times \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right] \cdot \left[\sum_L \frac{\mu_0}{4\pi}\vec{m}^L \times \frac{\left(\vec{r}_i - \vec{R}_L\right)}{|\vec{r}_i - \vec{R}_L|^3}\right]$$
$$+ 2\left[\frac{1}{2}\vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO})\right] \cdot \left[\sum_K \frac{\mu_0}{4\pi}\vec{m}^K \times \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right]$$

The first of the three terms was discussed in Exercise 5.5 and we found that

$$\left[\vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO})\right]^2 = \sum_{\alpha\beta} \mathcal{B}_\alpha \mathcal{B}_\beta \left[(r_i - R_{GO})^2 \delta_{\alpha\beta} - (r_{i,\alpha} - R_{GO,\alpha})(r_{i,\beta} - R_{GO,\beta})\right]$$

Using the same procedure as in Exercise 5.5, we get for the second term

$$\left[\sum_K \frac{\mu_0}{4\pi}\vec{m}^K \times \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right] \cdot \left[\sum_L \frac{\mu_0}{4\pi}\vec{m}^L \times \frac{\left(\vec{r}_i - \vec{R}_L\right)}{|\vec{r}_i - \vec{R}_L|^3}\right] =$$
$$\sum_{\alpha\beta}\sum_{KL} m_\alpha^K m_\beta^L \left[\frac{\left(\vec{r}_i - \vec{R}_L\right)}{|\vec{r}_i - \vec{R}_L|^3} \cdot \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\delta_{\alpha\beta} - \frac{(r_{i,\alpha} - R_{L,\alpha})}{|\vec{r}_i - \vec{R}_L|^3}\frac{(r_{i,\beta} - R_{K,\beta})}{|\vec{r}_i - \vec{R}_K|^3}\right]$$

which leads to the first contribution to the second contribution to the second-order perturbation Hamiltonian

$$\hat{H}^{(2)} = \sum_{KL}\sum_{\alpha\beta} \hat{O}_{\alpha\beta}^{m^K m^L} m_\alpha^K m_\beta^L$$

where

$$\hat{O}_{\alpha\beta}^{m^K m^L} = \frac{e^2}{2m_e}\left(\frac{\mu_0}{4\pi}\right)^2 \sum_i^N \left[\frac{\left(\vec{r}_i - \vec{R}_L\right)}{|\vec{r}_i - \vec{R}_L|^3} \cdot \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\delta_{\alpha\beta} - \frac{\left(\vec{r}_{i,\alpha} - \vec{R}_{L,\alpha}\right)}{|\vec{r}_i - \vec{R}_L|^3}\frac{\left(\vec{r}_{i,\beta} - \vec{R}_{K,\beta}\right)}{|\vec{r}_i - \vec{R}_K|^3}\right]$$

For the last term

$$\left[\vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO})\right] \cdot \left[\sum_K \frac{\mu_0}{4\pi}\vec{m}^K \times \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right]$$

one gets

$$\left[\vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO})\right] \cdot \left[\sum_K \frac{\mu_0}{4\pi} \vec{m}^K \times \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right] =$$

$$\left[\sum_K \frac{\mu_0}{4\pi} \vec{m}^K \times \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3}\right] \cdot \left[\vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO})\right] =$$

$$\sum_{\alpha\beta} m_\alpha^K \mathcal{B}_\beta \left[\left(\vec{r}_i - \vec{R}_{GO}\right) \cdot \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3} \delta_{\alpha\beta} - (r_{i,\alpha} - R_{GO,\alpha}) \frac{(r_{i,\beta} - R_{K,\beta})}{|\vec{r}_i - \vec{R}_K|^3}\right]$$

which leads to the third contribution to the second-order perturbation Hamiltonian

$$\hat{H}^{(2)} = \sum_{KL} \sum_{\alpha\beta} \hat{O}_{\alpha\beta}^{m^K \mathcal{B}} m_\alpha^K \mathcal{B}_\beta$$

where

$$\hat{O}_{\alpha\beta}^{m^K \mathcal{B}}(\vec{R}_{GO}) = \frac{e^2}{2m_e} \frac{\mu_0}{4\pi} \sum_i^N \left[\left(\vec{r}_i - \vec{R}_{GO}\right) \cdot \frac{\left(\vec{r}_i - \vec{R}_K\right)}{|\vec{r}_i - \vec{R}_K|^3} \delta_{\alpha\beta} - (r_{i,\alpha} - R_{GO,\alpha}) \frac{(r_{i,\beta} - R_{K,\beta})}{|\vec{r}_i - \vec{R}_K|^3}\right]$$

5.9 We are dealing with operators that are defined as

$$\hat{O}_\alpha^r = \sum_i^N r_{i,\alpha}$$

$$\hat{O}_\alpha^p = \sum_i^N p_{i,\alpha}$$

$$\hat{\mu}_\alpha(\vec{R}_{GO}) = -e \sum_i^N (r_{i,\alpha} - R_{GO,\alpha})$$

$$\hat{O}_\alpha^\mu(\vec{R}_K) = \frac{e}{4\pi\epsilon_0} \sum_i^N \frac{(r_{i,\alpha} - R_{K,\alpha})}{|\vec{r}_i - \vec{R}_K|^3}$$

First we want to show that the two commutators $\left[\hat{\vec{\mu}}(\vec{R}_{GO}), (\hat{\vec{O}}^r)^T\right]$ and $\left[\hat{\vec{O}}^\mu(\vec{R}_K), (\hat{\vec{O}}^r)^T\right]$ are zero. Since none of the operators contain a derivative with respect to electronic coordinates, it its trivial to see that the commute.

Using the vector triple product rule

$$\vec{A} \times \left(\vec{B} \times \vec{C}\right) = \vec{B}\left(\vec{A} \cdot \vec{C}\right) - \left(\vec{A} \cdot \vec{B}\right) \vec{C}$$

we can write the commutator

$$\left[\hat{\vec{O}}_2 \times \left(\hat{\vec{O}}_1 \times \hat{\vec{O}}^p\right), (\hat{\vec{O}}^r)^T\right]$$

as

$$\begin{aligned}
\left[\hat{\vec{O}}_2 \times \left(\hat{\vec{O}}_1 \times \hat{\vec{O}}^p\right), (\hat{\vec{O}}^r)^T\right] &= \left[\hat{\vec{O}}_1 \left(\hat{\vec{O}}_2 \cdot \hat{\vec{O}}^p\right), (\hat{\vec{O}}^r)^T\right] - \left[\left(\hat{\vec{O}}_1 \cdot \hat{\vec{O}}_2\right) \hat{\vec{O}}^p, (\hat{\vec{O}}^r)^T\right] \\
&= \left[\hat{\vec{O}}_1, (\hat{\vec{O}}^r)^T\right] \left(\hat{\vec{O}}_2 \cdot \hat{\vec{O}}^p\right) + \hat{\vec{O}}_1 \left[\hat{\vec{O}}_2 \cdot \hat{\vec{O}}^p, (\hat{\vec{O}}^r)^T\right] \\
&\quad - \left(\hat{\vec{O}}_1 \cdot \hat{\vec{O}}_2\right) \left[\hat{\vec{O}}^p, (\hat{\vec{O}}^r)^T\right] - \left[\hat{\vec{O}}_1 \cdot \hat{\vec{O}}_2, (\hat{\vec{O}}^r)^T\right] \hat{\vec{O}}^p
\end{aligned}$$

The first and the last commutators are zero as discussed before and the second commutator can be rewritten as

$$\left[\hat{\vec{O}}_2 \times \left(\hat{\vec{O}}_1 \times \hat{\vec{O}}^p\right), (\hat{\vec{O}}^r)^T\right] = \hat{\vec{O}}_1 (\hat{\vec{O}}_2)^T \; \left[\hat{\vec{O}}^p, (\hat{\vec{O}}^r)^T\right] - \left(\hat{\vec{O}}_2 \cdot \hat{\vec{O}}_1\right) \left[\hat{\vec{O}}^p, (\hat{\vec{O}}^r)^T\right]$$

Realizing that $\left[\hat{\vec{O}}^p, (\hat{\vec{O}}^r)^T\right]$ is in reality a matrix $\mathbf{M}$ of commutators with elements

$$M_{\alpha\beta} = \left[\hat{O}^p_\alpha, \hat{O}^r_\beta\right] = -\imath\hbar\delta_{\alpha\beta}$$

we finally obtain

$$-\frac{\imath}{\hbar} \left[\hat{\vec{O}}_2 \times \left(\hat{\vec{O}}_1 \times \hat{\vec{O}}^p\right), (\hat{\vec{O}}^r)^T\right] = -\hat{\vec{O}}_1 \otimes \hat{\vec{O}}_2 + \left(\hat{\vec{O}}_2 \cdot \hat{\vec{O}}_1\right) \mathbf{I}_3$$

5.10 The elements of the two tensors are defined as

$$\begin{aligned}
\xi_{\alpha\beta} = &- \langle \Psi_0^{(0)} | \hat{O}^{\mathcal{BB}}_{\alpha\beta}(\vec{R}_{GO}) + \hat{O}^{\mathcal{BB}}_{\beta\alpha}(\vec{R}_{GO}) | \Psi_0^{(0)} \rangle \\
&- \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} | \hat{m}^l_\alpha(\vec{R}_{GO}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{m}^l_\beta(\vec{R}_{GO}) | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \\
&- \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} | \hat{m}^l_\beta(\vec{R}_{GO}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{m}^l_\alpha(\vec{R}_{GO}) | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}
\end{aligned}$$

and

$$\begin{aligned}
\sigma^K_{\alpha\beta} = &\langle \Psi_0^{(0)} | \hat{O}^{m^K \mathcal{B}}_{\alpha\beta}(\vec{R}_{GO}) | \Psi_0^{(0)} \rangle \\
&+ \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} | \hat{O}^{OP}_{K,\alpha} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{m}^l_\beta(\vec{R}_{GO}) | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \\
&+ \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} | \hat{m}^l_\beta(\vec{R}_{GO}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{O}^{OP}_{K,\alpha} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}
\end{aligned}$$

We add now an arbitrary displacement vector $\vec{D}$ to the gauge origin $\vec{R}_{GO}$. If the sum of the dia- and paramagnetic terms are independent of the gauge origin, the terms containing this change should cancel.

Let us start with the nuclear magnetic shielding tensor:

$$\begin{aligned}
\sigma^K_{\alpha\beta} &= \langle\Psi_0^{(0)}|\hat{O}^{m^K\mathcal{B}}_{\alpha\beta}(\vec{R}_{GO}+\vec{D})|\Psi_0^{(0)}\rangle \\
&\quad+\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}|\hat{O}^{OP}_{K,\alpha}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{m}^l_\beta(\vec{R}_{GO}+\vec{D})|\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}} \\
&\quad+\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}|\hat{m}^l_\beta(\vec{R}_{GO}+\vec{D})|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}^{OP}_{K,\alpha}|\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}
\end{aligned}$$

where according to Eq. (5.21) and Eq. (3.65) the magnetic dipole moment operator for a shifted gauge origin can be written as

$$\begin{aligned}
\hat{m}^l_\alpha(\vec{R}_{GO}+\vec{D}) &= -\frac{e}{2m_e}\sum_i^N\left[(\vec{r}_i-\vec{R}_{GO}-\vec{D})\times\hat{\vec{p}}_i\right]_\alpha \\
&= \hat{m}^l_\alpha(\vec{R}_{GO})+\frac{e}{2m_e}\sum_i^N\left(\vec{D}\times\hat{\vec{p}}_i\right)_\alpha \\
&= \hat{m}^l_\alpha(\vec{R}_{GO})+\frac{e}{2m_e}\left(\vec{D}\times\hat{\vec{O}}^p\right)_\alpha
\end{aligned}$$

and according to Eq. (5.83) diamagnetic shielding operator becomes

$$\begin{aligned}
\hat{O}^{m^K\mathcal{B}}_{\alpha\beta}(\vec{R}_{GO}+\vec{D}) &= \frac{e^2}{2m_e}\frac{\mu_0}{4\pi}\sum_i^N\left(\vec{r}_i-\vec{R}_{GO}-\vec{D}\right)\cdot\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\,\delta_{\alpha\beta} \\
&\quad-\frac{e^2}{2m_e}\frac{\mu_0}{4\pi}\sum_i^N\left(r_{i,\alpha}-R_{GO,\alpha}-D_\alpha\right)\frac{r_{i,\beta}-R_{K,\beta}}{|\vec{r}_i-\vec{R}_K|^3} \\
&= \hat{O}^{m^K\mathcal{B}}_{\alpha\beta}(\vec{R}_{GO})-\frac{e^2}{2m_e}\frac{\mu_0}{4\pi}\sum_i^N\left(\vec{D}\cdot\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\,\delta_{\alpha\beta}-D_\alpha\frac{r_{i,\beta}-R_{K,\beta}}{|\vec{r}_i-\vec{R}_K|^3}\right)
\end{aligned}$$

Inserting the last expressions for both operators in the equation for the elements of the nuclear magnetic shielding tensor, we get

$$\begin{aligned}
\sigma^K_{\alpha\beta} &= \langle\Psi_0^{(0)}|\hat{O}^{m^K\mathcal{B}}_{\alpha\beta}(\vec{R}_{GO})|\Psi_0^{(0)}\rangle \\
&\quad+\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}|\hat{O}^{OP}_{K,\alpha}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{m}^l_\beta(\vec{R}_{GO})|\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}} \\
&\quad+\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}|\hat{m}^l_\beta(\vec{R}_{GO})|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}^{OP}_{K,\alpha}|\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}
\end{aligned}$$

plus the following contributions

$$
\begin{aligned}
&- \frac{e^2}{2m_e}\frac{\mu_0}{4\pi}\langle\Psi_0^{(0)}|\sum_i^N\left(\vec{D}\cdot\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\,\delta_{\alpha\beta}-D_\alpha\frac{r_{i,\beta}-R_{K,\beta}}{|\vec{r}_i-\vec{R}_K|^3}\right)|\Psi_0^{(0)}\rangle\\
&+\frac{e}{2m_e}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}|\hat{O}^{OP}_{K,\alpha}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\\
&+\frac{e}{2m_e}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}^{OP}_{K,\alpha}|\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}
\end{aligned}
$$

In order for the tensor to be independent of the gauge origin, the three last terms, which we denote as $\Delta\sigma^K_{\alpha\beta}$, must cancel. Using the off-diagonal hypervirial theorem, Eq. (3.66), we obtain

$$
\begin{aligned}
\Delta\sigma^K_{\alpha\beta} = &- \frac{e^2}{2m_e}\frac{\mu_0}{4\pi}\langle\Psi_0^{(0)}|\sum_i^N\left(\vec{D}\cdot\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\delta_{\alpha\beta}-D_\alpha\frac{r_{i,\beta}-R_{K,\beta}}{|\vec{r}_i-\vec{R}_K|^3}\right)|\Psi_0^{(0)}\rangle\\
&+\frac{e}{2\imath\hbar}\sum_{n\neq 0}\langle\Psi_0^{(0)}|\hat{O}^{OP}_{K,\alpha}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\left(\vec{D}\times\hat{\vec{O}}^r\right)_\beta|\Psi_0^{(0)}\rangle\\
&-\frac{e}{2\imath\hbar}\sum_{n\neq 0}\langle\Psi_0^{(0)}|\left(\vec{D}\times\hat{\vec{O}}^r\right)_\beta|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}^{OP}_{K,\alpha}|\Psi_0^{(0)}\rangle
\end{aligned}
$$

Using Eq. (3.67) and the resolution of the identity, $\sum_n|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}| = 1$, we get

$$
\begin{aligned}
\Delta\sigma^K_{\alpha\beta} = &- \frac{e^2}{2m_e}\frac{\mu_0}{4\pi}\langle\Psi_0^{(0)}|\sum_i^N\left(\vec{D}\cdot\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\delta_{\alpha\beta}-D_\alpha\frac{r_{i,\beta}-R_{K,\beta}}{|\vec{r}_i-\vec{R}_K|^3}\right)|\Psi_0^{(0)}\rangle\\
&+\frac{e}{2\imath\hbar}\langle\Psi_0^{(0)}|\hat{O}^{OP}_{K,\alpha}\left(\vec{D}\times\hat{\vec{O}}^r\right)_\beta|\Psi_0^{(0)}\rangle-\frac{e}{2\imath\hbar}\langle\Psi_0^{(0)}|\left(\vec{D}\times\hat{\vec{O}}^r\right)_\beta\hat{O}^{OP}_{K,\alpha}|\Psi_0^{(0)}\rangle
\end{aligned}
$$

or

$$
\begin{aligned}
\Delta\sigma^K_{\alpha\beta} = &- \frac{e^2}{2m_e}\frac{\mu_0}{4\pi}\langle\Psi_0^{(0)}|\sum_i^N\left(\vec{D}\cdot\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\delta_{\alpha\beta}-D_\alpha\frac{r_{i,\beta}-R_{K,\beta}}{|\vec{r}_i-\vec{R}_K|^3}\right)|\Psi_0^{(0)}\rangle\\
&+\frac{e}{2\imath\hbar}\langle\Psi_0^{(0)}|\left[\hat{O}^{OP}_{K,\alpha},\left(\vec{D}\times\hat{\vec{O}}^r\right)_\beta\right]|\Psi_0^{(0)}\rangle
\end{aligned}
$$

The operator $\hat{O}^{OP}_{K,\alpha}$ is given by

$$
\hat{O}^{OP}_{K,\alpha} = -\frac{e}{m_e}\frac{\mu_0}{4\pi}\sum_i^N\frac{\hat{l}_{i,\alpha}(R_K)}{|\vec{r}_i-\vec{R}_K|^3} = -\frac{e}{m_e}\frac{\mu_0}{4\pi}\sum_i^N\left(\frac{\vec{r}_i-\vec{R}_K}{|\,\vec{r}_i-\vec{R}_K\,|^3}\times\hat{\vec{p}}_i\right)_\alpha
$$

which results in

$$\Delta\sigma^K_{\alpha\beta} = -\frac{e^2}{2m_e}\frac{\mu_0}{4\pi}\langle\Psi_0^{(0)}|\sum_i^N\left(\vec{D}\cdot\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\delta_{\alpha\beta} - D_\alpha\frac{r_{i,\beta}-R_{K,\beta}}{|\vec{r}_i-\vec{R}_K|^3}\right)|\Psi_0^{(0)}\rangle$$
$$-\frac{e^2}{2m_e\imath\hbar}\frac{\mu_0}{4\pi}\langle\Psi_0^{(0)}|\left[\sum_i^N\left(\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\times\hat{\vec{p}}_i\right)_\alpha, \left(\vec{D}\times\hat{\vec{O}}^r\right)_\beta\right]|\Psi_0^{(0)}\rangle$$

Before we evaluate the commutator and corresponding ones for the magnetizability later on, it is useful to proof first the following general commutator relation

$$\left[\left(\vec{C}\times\sum_i\hat{\vec{r}}_i\right)_\alpha, \left(\sum_j\hat{\vec{o}}_j\times\hat{\vec{p}}_j\right)_\beta\right] = \imath\hbar\sum_i\left(\hat{\vec{o}}_i\cdot\vec{C}\,\boldsymbol{I}_3 - \hat{\vec{o}}_i\otimes\vec{C}\right)_{\alpha\beta}$$

where the operator $\hat{\vec{o}}_i$ commutes with $\hat{\vec{r}}_i$, i.e. $[\hat{o}_{i,\alpha},\hat{r}_{i,\beta}] = 0$ and $\vec{C}$ is a constant vector. We don't need to consider the case, where the two operators $\hat{\vec{r}}_i$ and $\hat{\vec{o}}_j\times\hat{\vec{p}}_j$ refer to different electrons, as the commutator is always zero then and we will drop the electron index i during the proof of this commutator. In order to do proof the commutator, it is best to distinguish between the two cases $\alpha = \beta$ and $\alpha \neq \beta$ and to consider two particular components like xx and xy. For $\alpha = \beta = x$ the commutator becomes then

$$\left[\left(\vec{C}\times\hat{\vec{r}}\right)_x, \left(\hat{\vec{o}}\times\hat{\vec{p}}\right)_x\right] = \hat{o}_y\hat{C}_y\,[\hat{r}_z,\hat{p}_z] + \hat{o}_z\hat{C}_z\,[\hat{r}_y,\hat{p}_y]$$

Using that $[\hat{r}_\alpha,\hat{p}_\beta] = \imath\hbar\;\delta_{\alpha\beta}$ one obtains

$$\left[\left(\vec{C}\times\hat{\vec{r}}\right)_x, \left(\hat{\vec{o}}\times\hat{\vec{p}}\right)_x\right] = \imath\hbar\left(\hat{o}_y\hat{C}_y + \hat{o}_z\hat{C}_z\right)$$

For $\alpha = x$ and $\beta = y$ the commutator becomes correspondingly

$$\left[\left(\vec{C}\times\hat{\vec{r}}\right)_x, \left(\hat{\vec{o}}\times\hat{\vec{p}}\right)_y\right] = -\hat{o}_x\hat{C}_y\,[\hat{r}_z,\hat{p}_z] = -\imath\hbar\;\hat{o}_x\hat{C}_y$$

The same holds then for all the other components, which proofs the commutator relation above.

Applying the commutator now to the case of the shielding tensor, gives for $\Delta\sigma^K_{\alpha\beta}$

$$\Delta\sigma^K_{\alpha\beta} = -\frac{e^2}{2m_e}\frac{\mu_0}{4\pi}\langle\Psi_0^{(0)}|\sum_i^N\left(\vec{D}\cdot\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\delta_{\alpha\beta} - D_\alpha\frac{r_{i,\beta}-R_{K,\beta}}{|\vec{r}_i-\vec{R}_K|^3}\right)|\Psi_0^{(0)}\rangle$$
$$-\frac{e^2}{2m_e\imath\hbar}\frac{\mu_0}{4\pi}\,(-\imath\hbar)\,\langle\Psi_0^{(0)}|\sum_i^N\left(\vec{D}\cdot\frac{\vec{r}_i-\vec{R}_K}{|\vec{r}_i-\vec{R}_K|^3}\delta_{\alpha\beta} - D_\alpha\frac{r_{i,\beta}-R_{K,\beta}}{|\vec{r}_i-\vec{R}_K|^3}\right)|\Psi_0^{(0)}\rangle$$
$$= 0$$

which is what we wanted to show.

For the magnetizability tensor we get correspondingly on displacing the gauge origin $\vec{R}_{GO}$ by $\vec{D}$

$$\xi_{\alpha\beta} = -\langle \Psi_0^{(0)} | \hat{O}^{\mathcal{BB}}_{\alpha\beta}(\vec{R}_{GO}+\vec{D}) + \hat{O}^{\mathcal{BB}}_{\beta\alpha}(\vec{R}_{GO}+\vec{D}) | \Psi_0^{(0)} \rangle$$
$$- \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} | \hat{m}^l_\alpha(\vec{R}_{GO}+\vec{D}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{m}^l_\beta(\vec{R}_{GO}+\vec{D}) | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}$$
$$- \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} | \hat{m}^l_\beta(\vec{R}_{GO}+\vec{D}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{m}^l_\alpha(\vec{R}_{GO}+\vec{D}) | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}$$

where

$$\hat{O}^{\mathcal{BB}}_{\alpha\beta}(\vec{R}_{GO}+\vec{D})$$
$$= \frac{e^2}{8m_e} \sum_i^N \left[\left(\vec{r}_i - \vec{R}_{GO} - \vec{D}\right)^2 \delta_{\alpha\beta} - (r_{i,\alpha} - R_{GO,\alpha} - D_\alpha)\,(r_{i,\beta} - R_{GO,\beta} - D_\beta) \right]$$
$$= \hat{O}^{\mathcal{BB}}_{\alpha\beta}(\vec{R}_{GO}) + \frac{e^2}{8m_e}\left(\vec{D}^2\delta_{\alpha\beta} - D_\alpha D_\beta\right) - \frac{e^2}{8m_e}\sum_i^N \left[\left(\vec{r}_i - \vec{R}_{GO}\right)\cdot\vec{D}\,\delta_{\alpha\beta} - D_\alpha\,(r_{i,\beta} - R_{GO,\beta})\right]$$
$$- \frac{e^2}{8m_e}\sum_i^N \left[\vec{D}\cdot\left(\vec{r}_i - \vec{R}_{GO}\right)\,\delta_{\alpha\beta} - (r_{i,\alpha} - R_{GO,\alpha})\,D_\beta\right]$$

Inserting this and the expression for $\hat{m}^l_\alpha(\vec{R}_{GO}+\vec{D})$ from above in the expression for the magnetizability tensor one obtains

$$\xi_{\alpha\beta} = -\langle \Psi_0^{(0)} | \hat{O}^{\mathcal{BB}}_{\alpha\beta}(\vec{R}_{GO}) + \hat{O}^{\mathcal{BB}}_{\beta\alpha}(\vec{R}_{GO}) | \Psi_0^{(0)} \rangle$$
$$- \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} | \hat{m}^l_\alpha(\vec{R}_{GO}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{m}^l_\beta(\vec{R}_{GO}) | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}$$
$$- \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} | \hat{m}^l_\beta(\vec{R}_{GO}) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{m}^l_\alpha(\vec{R}_{GO}) | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}$$
$$- \frac{e^2}{4m_e}\langle \Psi_0^{(0)} | \left(\vec{D}^2\delta_{\alpha\beta} - D_\alpha D_\beta\right) | \Psi_0^{(0)} \rangle$$
$$+ \frac{e^2}{4m_e}\langle \Psi_0^{(0)} | \sum_i^N \left[\left(\vec{r}_i - \vec{R}_{GO}\right)\cdot\vec{D}\,\delta_{\alpha\beta} - D_\alpha\,(r_{i,\beta} - R_{GO,\beta})\right] | \Psi_0^{(0)} \rangle$$
$$+ \frac{e^2}{4m_e}\langle \Psi_0^{(0)} | \sum_i^N \left[\vec{D}\cdot\left(\vec{r}_i - \vec{R}_{GO}\right)\,\delta_{\alpha\beta} - (r_{i,\alpha} - R_{GO,\alpha})\,D_\beta\right] | \Psi_0^{(0)} \rangle$$

plus the following contributions

$$
\begin{aligned}
&- \frac{e^2}{4m_e^2} \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\alpha \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\beta \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \\
&- \frac{e^2}{4m_e^2} \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\beta \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\alpha \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \\
&+ \frac{e}{2m_e} \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{m}^l_\alpha(\vec{R}_{GO}) \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\beta \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \\
&+ \frac{e}{2m_e} \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{m}^l_\beta(\vec{R}_{GO}) \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\alpha \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \\
&+ \frac{e}{2m_e} \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\alpha \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{m}^l_\beta(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \\
&+ \frac{e}{2m_e} \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\beta \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{m}^l_\alpha(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}
\end{aligned}
$$

The last nine terms, which we will denote $\Delta\xi_{\alpha\beta}$, must be zero in order for the magnetizability tensor to be independent of the gauge origin. Using the off-diagonal hypervirial theorem we get for them

$$
\begin{aligned}
\Delta\xi_{\alpha\beta} = &- \frac{e^2}{4m_e} \langle \Psi_0^{(0)} \,|\, \left(\vec{D}^2 \delta_{\alpha\beta} - D_\alpha D_\beta\right) \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e^2}{4m_e} \langle \Psi_0^{(0)} \,|\, \sum_i^N \left[\left(\vec{r}_i - \vec{R}_{GO}\right) \cdot \vec{D}\, \delta_{\alpha\beta} - D_\alpha \left(r_{i,\beta} - R_{GO,\beta}\right) \right] \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e^2}{4m_e} \langle \Psi_0^{(0)} \,|\, \sum_i^N \left[\vec{D} \cdot \left(\vec{r}_i - \vec{R}_{GO}\right) \delta_{\alpha\beta} - \left(r_{i,\alpha} - R_{GO,\alpha}\right) D_\beta \right] \,|\, \Psi_0^{(0)} \rangle \\
&- \frac{e^2}{4m_e \imath\hbar} \sum_{n\neq 0} \langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\alpha \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e^2}{4m_e \imath\hbar} \sum_{n\neq 0} \langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\alpha \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e}{2\imath\hbar} \sum_{n\neq 0} \langle \Psi_0^{(0)} \,|\, \hat{m}^l_\alpha(\vec{R}_{GO}) \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta \,|\, \Psi_0^{(0)} \rangle
\end{aligned}
$$

plus the following contributions

$$+ \frac{e}{2\imath\hbar} \sum_{n\neq 0} \langle \Psi_0^{(0)} \,|\, \hat{m}^l_\beta(\vec{R}_{GO}) \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\alpha \,|\, \Psi_0^{(0)} \rangle$$

$$- \frac{e}{2\imath\hbar} \sum_{n\neq 0} \langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\alpha \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{m}^l_\beta(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle$$

$$- \frac{e}{2\imath\hbar} \sum_{n\neq 0} \langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{m}^l_\alpha(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle$$

Using again Eq. (3.67) and the resolution of the identity, $\sum_n |\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}| = 1$, we get

$$\begin{aligned}
\Delta\xi_{\alpha\beta} = &- \frac{e^2}{4m_e} \langle \Psi_0^{(0)} \,|\, \left(\vec{D}^2 \delta_{\alpha\beta} - D_\alpha D_\beta\right) \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e^2}{4m_e} \langle \Psi_0^{(0)} \,|\, \sum_i^N \left[\left(\vec{r}_i - \vec{R}_{GO}\right) \cdot \vec{D}\, \delta_{\alpha\beta} - D_\alpha \left(r_{i,\beta} - R_{GO,\beta}\right)\right] \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e^2}{4m_e} \langle \Psi_0^{(0)} \,|\, \sum_i^N \left[\vec{D} \cdot \left(\vec{r}_i - \vec{R}_{GO}\right) \delta_{\alpha\beta} - \left(r_{i,\alpha} - R_{GO,\alpha}\right) D_\beta\right] \,|\, \Psi_0^{(0)} \rangle \\
&- \frac{e^2}{4m_e\imath\hbar} \langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^p\right)_\alpha \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e^2}{4m_e\imath\hbar} \langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta \left(\vec{D} \times \hat{\vec{O}}^p\right)_\alpha \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e}{2\imath\hbar} \langle \Psi_0^{(0)} \,|\, \hat{m}^l_\alpha(\vec{R}_{GO}) \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta \,|\, \Psi_0^{(0)} \rangle - \frac{e}{2\imath\hbar} \langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta \hat{m}^l_\alpha(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e}{2\imath\hbar} \langle \Psi_0^{(0)} \,|\, \hat{m}^l_\beta(\vec{R}_{GO}) \left(\vec{D} \times \hat{\vec{O}}^r\right)_\alpha \,|\, \Psi_0^{(0)} \rangle - \frac{e}{2\imath\hbar} \langle \Psi_0^{(0)} \,|\, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\alpha \hat{m}^l_\beta(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle
\end{aligned}$$

which can be rewritten as

$$\begin{aligned}
\Delta\xi_{\alpha\beta} = &- \frac{e^2}{4m_e} \langle \Psi_0^{(0)} \,|\, \left(\vec{D}^2 \delta_{\alpha\beta} - D_\alpha D_\beta\right) \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e^2}{4m_e} \langle \Psi_0^{(0)} \,|\, \sum_i^N \left[\left(\vec{r}_i - \vec{R}_{GO}\right) \cdot \vec{D}\, \delta_{\alpha\beta} - D_\alpha \left(r_{i,\beta} - R_{GO,\beta}\right)\right] \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e^2}{4m_e} \langle \Psi_0^{(0)} \,|\, \sum_i^N \left[\vec{D} \cdot \left(\vec{r}_i - \vec{R}_{GO}\right) \delta_{\alpha\beta} - \left(r_{i,\alpha} - R_{GO,\alpha}\right) D_\beta\right] \,|\, \Psi_0^{(0)} \rangle \\
&- \frac{e^2}{4m_e\imath\hbar} \langle \Psi_0^{(0)} \,|\, \left[\left(\vec{D} \times \hat{\vec{O}}^p\right)_\alpha, \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta\right] \,|\, \Psi_0^{(0)} \rangle \\
&+ \frac{e}{2\imath\hbar} \langle \Psi_0^{(0)} \,|\, \left[\hat{m}^l_\alpha(\vec{R}_{GO}), \left(\vec{D} \times \hat{\vec{O}}^r\right)_\beta\right] \,|\, \Psi_0^{(0)} \rangle + \frac{e}{2\imath\hbar} \langle \Psi_0^{(0)} \,|\, \left[\hat{m}^l_\beta(\vec{R}_{GO}), \left(\vec{D} \times \hat{\vec{O}}^r\right)_\alpha\right] \,|\, \Psi_0^{(0)} \rangle
\end{aligned}$$

Now we can apply the general commutator relation,

$$\left[\left(\vec{C} \times \sum_i \hat{\vec{r}}_i \right)_\alpha , \left(\sum_j \hat{\vec{o}}_j \times \hat{\vec{p}}_j \right)_\beta \right] = \imath\hbar \sum_i \left(\hat{\vec{o}}_i \cdot \vec{C} \, \boldsymbol{I}_3 - \hat{\vec{o}}_i \otimes \vec{C} \right)_{\alpha\beta}$$

again for all three commutators and obtain

$$\begin{aligned}
\Delta\xi_{\alpha\beta} = & -\frac{e^2}{4m_e} \langle \Psi_0^{(0)} | \left(\vec{D}^2 \delta_{\alpha\beta} - D_\alpha D_\beta \right) | \Psi_0^{(0)} \rangle \\
& + \frac{e^2}{4m_e} \langle \Psi_0^{(0)} | \sum_i^N \left[\left(\vec{r}_i - \vec{R}_{GO} \right) \cdot \vec{D} \, \delta_{\alpha\beta} - D_\alpha \left(r_{i,\beta} - R_{GO,\beta} \right) \right] | \Psi_0^{(0)} \rangle \\
& + \frac{e^2}{4m_e} \langle \Psi_0^{(0)} | \sum_i^N \left[\vec{D} \cdot \left(\vec{r}_i - \vec{R}_{GO} \right) \, \delta_{\alpha\beta} - \left(r_{i,\alpha} - R_{GO,\alpha} \right) D_\beta \right] | \Psi_0^{(0)} \rangle \\
& + \frac{e^2}{4m_e} \langle \Psi_0^{(0)} | \left(\vec{D}^2 \delta_{\alpha\beta} - D_\alpha D_\beta \right) | \Psi_0^{(0)} \rangle \\
& - \frac{e^2}{4m_e} \langle \Psi_0^{(0)} | \sum_i^N \left[\left(\vec{r}_i - \vec{R}_{GO} \right) \cdot \vec{D} \, \delta_{\alpha\beta} - D_\alpha \left(r_{i,\beta} - R_{GO,\beta} \right) \right] | \Psi_0^{(0)} \rangle \\
& - \frac{e^2}{4m_e} \langle \Psi_0^{(0)} | \sum_i^N \left[\vec{D} \cdot \left(\vec{r}_i - \vec{R}_{GO} \right) \, \delta_{\alpha\beta} - \left(r_{i,\alpha} - R_{GO,\alpha} \right) D_\beta \right] | \Psi_0^{(0)} \rangle \\
= & \; 0
\end{aligned}$$

which is, what we wanted to show.

5.11 We start from the intermediate result for the change in the shielding tensor due to a change in the gauge origin from Exercise 5.10

$$\begin{aligned}
\Delta\sigma^K_{\alpha\beta} = & -\frac{e^2}{2m_e} \frac{\mu_0}{4\pi} \langle \Psi_0^{(0)} | \sum_i^N \left(\vec{D} \cdot \frac{\vec{r}_i - \vec{R}_K}{|\vec{r}_i - \vec{R}_K|^3} \, \delta_{\alpha\beta} - D_\alpha \frac{r_{i,\beta} - R_{K,\beta}}{|\vec{r}_i - \vec{R}_K|^3} \right) | \Psi_0^{(0)} \rangle \\
& + \frac{e}{2m_e} \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{O}^{OP}_{K,\alpha} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \left(\vec{D} \times \hat{\vec{O}}^p \right)_\beta | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \\
& + \frac{e}{2m_e} \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \left(\vec{D} \times \hat{\vec{O}}^p \right)_\beta | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{O}^{OP}_{K,\alpha} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}
\end{aligned}$$

The change in the isotropic shielding constant becomes then

$$
\begin{aligned}
\Delta\sigma^K &= \frac{1}{3}\sum_{\alpha}\Delta\sigma^K_{\alpha\alpha}\\
&= -\frac{e^2}{3m_e}\frac{\mu_0}{4\pi}\sum_{\alpha} D_\alpha \langle\Psi_0^{(0)}\,|\sum_i^N \frac{r_{i,\alpha}-R_{K,\alpha}}{|\vec{r}_i-\vec{R}_K|^3}\,|\,\Psi_0^{(0)}\rangle\\
&\quad + \frac{e}{6m_e}\sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma}D_\alpha\left(\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^{OP}_{K,\gamma}\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^{p}_{\beta}\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right.\\
&\qquad\qquad\left.+\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^{p}_{\beta}\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^{OP}_{K,\gamma}\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right)
\end{aligned}
$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol as defined in Eq. (5.112). Using the definition of the electric-field gradient operator $\hat{O}^{\mu}_{\alpha}$ in Eq. (4.95) and the fact that $\epsilon_0\mu_0 = \frac{1}{c^2}$ we obtain

$$
\begin{aligned}
\Delta\sigma^K &= -\frac{e}{3m_e c^2}\sum_{\alpha} D_\alpha \langle\Psi_0^{(0)}\,|\,\hat{O}^{\mu}_{\alpha}(\vec{R}_K)\,|\,\Psi_0^{(0)}\rangle\\
&\quad + \frac{e}{6m_e}\sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma}D_\alpha\left(\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^{OP}_{K,\gamma}\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^{p}_{\beta}\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right.\\
&\qquad\qquad\left.+\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^{p}_{\beta}\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^{OP}_{K,\gamma}\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right)
\end{aligned}
$$

which implies that the components of the gauge-origin dependence vector for the shielding constant are given as

$$
\begin{aligned}
C^{\sigma}_{1,\alpha} &= \frac{e}{6m_e}\sum_{\beta\gamma}\epsilon_{\alpha\beta\gamma}\left(\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^{p}_{\beta}\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^{OP}_{K,\gamma}\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right.\\
&\qquad\qquad\left.+\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^{OP}_{K,\gamma}\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^{p}_{\beta}\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right)\\
&\quad - \frac{e}{3m_e c^2}\langle\Psi_0^{(0)}\,|\,\hat{O}^{\mu}_{\alpha}(\vec{R}_K)\,|\,\Psi_0^{(0)}\rangle
\end{aligned}
$$

For the magnetizability we obtained for the change in the tensor elements in Exercise 5.10

$$
\begin{aligned}
\Delta\xi_{\alpha\beta} = & -\frac{e^2}{4m_e}\langle\Psi_0^{(0)}\,|\left(\vec{D}^2\delta_{\alpha\beta} - D_\alpha D_\beta\right)|\,\Psi_0^{(0)}\rangle \\
& + \frac{e^2}{4m_e}\langle\Psi_0^{(0)}\,|\sum_i^N\left[\left(\vec{r}_i - \vec{R}_{GO}\right)\cdot\vec{D}\,\delta_{\alpha\beta} - D_\alpha\left(r_{i,\beta} - R_{GO,\beta}\right)\right]|\,\Psi_0^{(0)}\rangle \\
& + \frac{e^2}{4m_e}\langle\Psi_0^{(0)}\,|\sum_i^N\left[\vec{D}\cdot\left(\vec{r}_i - \vec{R}_{GO}\right)\,\delta_{\alpha\beta} - \left(r_{i,\alpha} - R_{GO,\alpha}\right)D_\beta\right]|\,\Psi_0^{(0)}\rangle \\
& - \frac{e^2}{4m_e^2}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\alpha|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}} \\
& - \frac{e^2}{4m_e^2}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\alpha|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}} \\
& + \frac{e}{2m_e}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{m}^l_\alpha(\vec{R}_{GO})\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}} \\
& + \frac{e}{2m_e}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{m}^l_\beta(\vec{R}_{GO})\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\alpha|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}} \\
& + \frac{e}{2m_e}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\alpha|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{m}^l_\beta(\vec{R}_{GO})\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}} \\
& + \frac{e}{2m_e}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{m}^l_\alpha(\vec{R}_{GO})\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}
\end{aligned}
$$

The change in the isotropic magnetizability becomes then

$$
\begin{aligned}
\Delta\xi = & -\frac{e^2}{6m_e}\langle\Psi_0^{(0)}\,|\,\vec{D}^2\,|\,\Psi_0^{(0)}\rangle + \frac{e^2}{3m_e}\langle\Psi_0^{(0)}\,|\sum_i^N\left(\vec{r}_i - \vec{R}_{GO}\right)|\,\Psi_0^{(0)}\rangle\cdot\vec{D} \\
& - \frac{e^2}{6m_e^2}\sum_{\alpha\beta}D_\alpha\left(\sum_\gamma\delta_{\alpha\beta}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^p_\gamma\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^p_\gamma\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\right. \\
& \left. - \sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^p_\beta\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^p_\alpha\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\right)D_\beta
\end{aligned}
$$

plus the following terms

$$+\frac{e}{3m_e}\sum_{\alpha} D_\alpha \sum_{\beta\gamma} \epsilon_{\alpha\beta\gamma} \left(\sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{m}^l_\gamma(\vec{R}_{GO}) \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{O}^p_\beta \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right.$$
$$\left. + \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{O}^p_\beta \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{m}^l_\gamma(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right)$$

Using the definition that the norm of the wavefunction is equal to the number of electrons, $\langle \Psi_0^{(0)} \mid \Psi_0^{(0)} \rangle = N$, and the definition of the electric dipole moment operator in Eq. (4.30) one obtains

$$\Delta\xi = -\frac{e^2}{6m_e}\vec{D}^2 N - \frac{e}{3m_e}\langle \Psi_0^{(0)} \,|\, \hat{\vec{\mu}}(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle \cdot \vec{D}$$
$$-\frac{e^2}{6m_e^2}\sum_{\alpha\beta} D_\alpha \left(\sum_{\gamma} \delta_{\alpha\beta} \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{O}^p_\gamma \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{O}^p_\gamma \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right.$$
$$\left. - \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{O}^p_\beta \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{O}^p_\alpha \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right) D_\beta$$
$$+\frac{e}{3m_e}\sum_{\alpha} D_\alpha \sum_{\beta\gamma} \epsilon_{\alpha\beta\gamma} \left(\sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{m}^l_\gamma(\vec{R}_{GO}) \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{O}^p_\beta \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right.$$
$$\left. + \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{O}^p_\beta \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{m}^l_\gamma(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right)$$

which implies that the components of the gauge-origin dependence vector for the magnetizability are given as

$$C^{\xi}_{1,\alpha}(\vec{R}_{GO}) = \frac{e}{3m_e}\sum_{\beta\gamma} \epsilon_{\alpha\beta\gamma} \left(\sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{O}^p_\beta \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{m}^l_\gamma(\vec{R}_{GO}) \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right.$$
$$\left. + \sum_{n\neq 0} \frac{\langle \Psi_0^{(0)} \,|\, \hat{m}^l_\gamma(\vec{R}_{GO}) \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{O}^p_\beta \,|\, \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \right)$$
$$-\frac{e}{3m_e}\langle \Psi_0^{(0)} \,|\, \hat{\mu}_\alpha(R_{GO}) \,|\, \Psi_0^{(0)} \rangle$$

$$C^{\xi}_{2,\alpha\beta} = -\frac{e^2}{6m_e^2}\left(\sum_\gamma \delta_{\alpha\beta}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^p_\gamma\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^p_\gamma\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right.$$
$$\left.-\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^p_\beta\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^p_\alpha\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right)$$
$$-\frac{e^2}{6m_e}N\delta_{\alpha\beta}$$

5.12 The change in the paramagnetic contribution to an element of the shielding tensor was derived in Exercise 5.10 to be

$$\Delta\sigma^{K,para}_{\alpha\beta} = \frac{e}{2m_e}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^{OP}_{K,\alpha}\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}$$
$$+\frac{e}{2m_e}\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^{OP}_{K,\alpha}\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}$$

Now we have to derive the corresponding change in the CTOCD-DZ diamagnetic contribution, Eq. (5.115). Let us start by deriving the change in $\hat{O}^{CTOCD-DZ}_{K,\delta\alpha}$, Eq. (5.117), on changing the gauge origin $\vec{R}_{GO}$ by $\vec{D}$. According to the definition of the electric dipole moment operator in Eq. (4.30), this becomes

$$\hat{O}^{CTOCD-DZ}_{K,\delta\alpha}(\vec{R}_{GO}+\vec{D}) = \frac{1}{4m_e}\left[\hat{\mu}_\delta(R_{GO}+\vec{D})\;\hat{O}^{OP}_{K,\alpha}+\hat{O}^{OP}_{K,\alpha}\;\hat{\mu}_\delta(R_{GO}+\vec{D})\right]$$
$$= \frac{1}{4m_e}\left[\hat{\mu}_\delta(R_{GO})\;\hat{O}^{OP}_{K,\alpha}+\hat{O}^{OP}_{K,\alpha}\;\hat{\mu}_\delta(R_{GO})\right]$$
$$+\frac{e}{4m_e}\left[D_\delta\;\hat{O}^{OP}_{K,\alpha}+\hat{O}^{OP}_{K,\alpha}\;D_\delta\right]$$

The change in the CTOCD-DZ diamagnetic contribution, Eq. (5.115), becomes then

$$\Delta\sigma^{K,\Delta}_{\alpha\beta} = \frac{e}{4m_e}\sum_{\gamma\delta}\epsilon_{\beta\gamma\delta}\left(\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\,\hat{O}^p_\gamma\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\left[D_\delta\;\hat{O}^{OP}_{K,\alpha}+\hat{O}^{OP}_{K,\alpha}\;D_\delta\right]|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right.$$
$$\left.+\sum_{n\neq 0}\frac{\langle\Psi_0^{(0)}\,|\left[D_\delta\;\hat{O}^{OP}_{K,\alpha}+\hat{O}^{OP}_{K,\alpha}\;D_\delta\right]|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{O}^p_\gamma\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right)$$

The displacement D_δ is a constant and can therefore be moved to the transition moments over $\hat{O}^p_\gamma$

$$\Delta\sigma^{K,\Delta}_{\alpha\beta} = \frac{e}{2m_e}\sum_{\gamma\delta}\epsilon_{\beta\gamma\delta}\left(\sum_{n\neq 0}\frac{\langle\Psi^{(0)}_0\,|\,\hat{O}^p_\gamma\ D_\delta\,|\,\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n\,|\,\hat{O}^{OP}_{K,\alpha}\,|\,\Psi^{(0)}_0\rangle}{E^{(0)}_0 - E^{(0)}_n}\right.$$
$$\left. + \sum_{n\neq 0}\frac{\langle\Psi^{(0)}_0\,|\,\hat{O}^{OP}_{K,\alpha}\,|\,\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n\,|\,\hat{O}^p_\gamma\ D_\delta\,|\,\Psi^{(0)}_0\rangle}{E^{(0)}_0 - E^{(0)}_n}\right)$$

Recognizing $\sum_{\gamma\delta}\epsilon_{\beta\gamma\delta}\hat{O}^p_\gamma\ D_\delta$ as the β component of the vector product $\hat{\vec{O}}^p \times \vec{D}$ we can rewrite it as

$$\Delta\sigma^{K,\Delta}_{\alpha\beta} = -\frac{e}{2m_e}\left(\sum_{n\neq 0}\frac{\langle\Psi^{(0)}_0\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\,\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n\,|\,\hat{O}^{OP}_{K,\alpha}\,|\,\Psi^{(0)}_0\rangle}{E^{(0)}_0 - E^{(0)}_n}\right.$$
$$\left. + \sum_{n\neq 0}\frac{\langle\Psi^{(0)}_0\,|\,\hat{O}^{OP}_{K,\alpha}\,|\,\Psi^{(0)}_n\rangle\langle\Psi^{(0)}_n\,|\left(\vec{D}\times\hat{\vec{O}}^p\right)_\beta|\,\Psi^{(0)}_0\rangle}{E^{(0)}_0 - E^{(0)}_n}\right)$$

which cancels exactly the change in the paramagnetic contribution.

Solutions to Chapter 6

6.1 We can proof this by looking at only one component, e.g. the x-component, $\left[\vec{A} \times \left(\vec{B} \times \vec{C}\right)\right]_x$, which is

$$\left[\vec{A} \times \left(\vec{B} \times \vec{C}\right)\right]_x = A_y \left(\vec{B} \times \vec{C}\right)_z - A_z \left(\vec{B} \times \vec{C}\right)_y$$

Evaluating the inner vector product gives then

$$\left[\vec{A} \times \left(\vec{B} \times \vec{C}\right)\right]_x = A_y \left(B_x C_y - B_y C_x\right) - A_z \left(B_z C_x - B_x C_z\right)$$

which can be rewritten as

$$\left[\vec{A} \times \left(\vec{B} \times \vec{C}\right)\right]_x = B_x \left(A_y C_y + A_z C_z\right) - \left(A_y B_y + A_z B_z\right) C_x$$

Adding and subtracting then $A_x B_x C_x$ we get

$$\left[\vec{A} \times \left(\vec{B} \times \vec{C}\right)\right]_x = B_x \left(A_x C_x + A_y C_y + A_z C_z\right) - \left(A_x B_x + A_y B_y + A_z B_z\right) C_x$$

which is the same as

$$\left[\vec{A} \times \left(\vec{B} \times \vec{C}\right)\right]_x = B_x \left(A \cdot C\right) - \left(A \cdot B\right) C_x$$

and thus the x-component of

$$\left[\vec{A} \times \left(\vec{B} \times \vec{C}\right)\right]_x = \left[\vec{B}\left(\vec{A} \cdot \vec{C}\right) - \left(\vec{A} \cdot \vec{B}\right) \vec{C}\right]_x$$

The same can be shown also for the other two components.

6.2 The second-order molecular Hamiltonian reads for magnetic perturbations

$$\hat{H}^{(2)} = \sum_i^N \hat{h}^{(2)}(i)$$

with

$$\hat{h}^{(2)}(i) = \frac{e^2}{2m_e} \hat{\vec{A}}^2(\vec{r}_i)$$

The relevant vector potentials are given in (5.19) and (6.5)

$$\hat{\vec{A}} = \hat{\vec{A}}^J + \hat{\vec{A}}^{\mathcal{B}}$$

where

$$\hat{\vec{A}}^J = -\frac{m_e}{e} \boldsymbol{I}^{-1} \vec{J} \times \left(\vec{r} - \vec{R}_{CM}\right)$$

$$\hat{\vec{A}}^{\mathcal{B}} = \frac{1}{2} \vec{\mathcal{B}} \times \left(\vec{r}_i - \vec{R}_{GO}\right)$$

The square of the vector potential becomes then

$$\hat{\vec{A}}^2 = \left(\hat{\vec{A}}^J\right)^2 + \left(\hat{\vec{A}}^{\mathcal{B}}\right)^2 + 2\hat{\vec{A}}^J \cdot \hat{\vec{A}}^{\mathcal{B}}$$

The second-order perturbation Hamiltonian for the induced contribution to the rotational g tensor arises from the last term, which we can write as

$$\hat{h}^{(2)}(i) = \frac{e^2}{m_e}\left[-\frac{m_e}{e}\boldsymbol{I}^{-1}\vec{J} \times (\vec{r} - \vec{R}_{CM})\right] \cdot \left[\frac{1}{2}\vec{\mathcal{B}} \times (\vec{r}_i - \vec{R}_{GO})\right]$$

If we use again the relation

$$(\vec{A} \times \vec{B})(\vec{C} \times \vec{D}) = \vec{A}\,(\vec{D} \cdot \vec{B}\,\boldsymbol{I}_3 - \vec{D}\vec{B}^T)\,\vec{C}$$

the second-order operator becomes

$$\hat{h}^{(2)}(i) = -\frac{e}{2}\sum_{\alpha\beta}\mathcal{B}_\alpha \left[(\vec{r}_i - \vec{R}_{CM}) \cdot (\vec{r}_i - \vec{R}_{GO})\delta_{\alpha\beta} - (r_{i,\alpha} - R_{CM,\alpha})(r_{i,\beta} - R_{GO,\beta})\right]\left(\boldsymbol{I}^{-1}\vec{J}\right)_\beta$$

which leads to the second-order perturbation Hamiltonian

$$\begin{aligned}\hat{H}^{(2)} &= \sum_i^N \hat{h}^{(2)}(i) \\ &= \sum_{\alpha\beta} \hat{O}^{\mathcal{B}J}_{\alpha\beta}(\vec{R}_{CM}, \vec{R}_{GO})\ \mathcal{B}_\alpha(\boldsymbol{I}^{-1}\ \vec{J})_\beta\end{aligned}$$

where

$$\hat{O}^{\mathcal{B}J}_{\alpha\beta}(\vec{R}_{CM}, \vec{R}_{GO}) = -\frac{e}{2}\sum_i^N \left[(\vec{r}_i - \vec{R}_{CM}) \cdot (\vec{r}_i - \vec{R}_{GO})\delta_{\alpha\beta} - (r_{i,\alpha} - R_{CM,\alpha})(r_{i,\beta} - R_{GO,\beta})\right]$$

6.3 Realizing that $\left[\vec{C} \times \hat{\vec{O}}^r, \left(\hat{\vec{\mu}}(\vec{R}_O) \times \hat{\vec{O}}^p\right)^T\right]$ is in reality a matrix of commutators we will show that it is equal to $\imath\hbar\left\{\hat{\vec{\mu}}(\vec{R}_O) \cdot \vec{C}\ \boldsymbol{I}_3 - \hat{\vec{\mu}}(\vec{R}_O) \otimes \vec{C}\right\}$ for both a diagonal element and an off-diagonal element. Expanding therefore the xx-element we have

$$\begin{aligned}\left[\vec{C} \times \hat{\vec{O}}^r, \left(\hat{\vec{\mu}}(\vec{R}_O) \times \hat{\vec{O}}^p\right)^T\right]_{xx} &= \left[\left(\vec{C} \times \hat{\vec{O}}^r\right)_x, \left(\hat{\vec{\mu}}(\vec{R}_O) \times \hat{\vec{O}}^p\right)_x\right] \\ &= \left[C_y\hat{O}^r_z - C_z\hat{O}^r_y, \hat{\mu}_y(\vec{R}_O)\hat{O}^p_z - \hat{\mu}_z(\vec{R}_O)\hat{O}^p_y\right] \\ &= \left[C_y\hat{O}^r_z, \hat{\mu}_y(\vec{R}_O)\hat{O}^p_z\right] - \left[C_y\hat{O}^r_z, \hat{\mu}_z(\vec{R}_O)\hat{O}^p_y\right] \\ &\quad - \left[C_z\hat{O}^r_y, \hat{\mu}_y(\vec{R}_O)\hat{O}^p_z\right] + \left[C_z\hat{O}^r_y, \hat{\mu}_z(\vec{R}_O)\hat{O}^p_y\right]\end{aligned}$$

But the components of the $\vec{C}$ are constants and any component of $\hat{\vec{\mu}}(\vec{R}_O)$ commutes with any component of $\hat{\vec{O}}^r$ and we can therefore take them out of the commutator

$$\left[\vec{C} \times \hat{\vec{O}}^r, \left(\hat{\vec{\mu}}(\vec{R}_O) \times \hat{\vec{O}}^p\right)^T\right]_{xx} = C_y \hat{\mu}_y(\vec{R}_O) \left[\hat{O}^r_z, \hat{O}^p_z\right] - C_y \hat{\mu}_z(\vec{R}_O) \left[\hat{O}^r_z, \hat{O}^p_y\right] - C_z \hat{\mu}_y(\vec{R}_O) \left[\hat{O}^r_y, \hat{O}^p_z\right] + C_z \hat{\mu}_z(\vec{R}_O) \left[\hat{O}^r_y, \hat{O}^p_y\right]$$

Evaluating the commutators $\left[\hat{O}^r_\alpha, \hat{O}^p_\beta\right] = \imath\hbar\delta_{\alpha\beta}$ leads to

$$\begin{aligned}\left[\vec{C} \times \hat{\vec{O}}^r, \left(\hat{\vec{\mu}}(\vec{R}_O) \times \hat{\vec{O}}^p\right)^T\right]_{xx} &= \imath\hbar C_y \hat{\mu}_y(\vec{R}_O) + \imath\hbar C_z \hat{\mu}_z(\vec{R}_O) \\ &= \imath\hbar \left\{\hat{\vec{\mu}}(\vec{R}_O) \cdot \vec{C}\ \boldsymbol{I}_3 - \hat{\vec{\mu}}(\vec{R}_O) \otimes \vec{C}\right\}_{xx}\end{aligned}$$

For the xy-element we obtain then analogously

$$\begin{aligned}\left[\vec{C} \times \hat{\vec{O}}^r, \left(\hat{\vec{\mu}}(\vec{R}_O) \times \hat{\vec{O}}^p\right)^T\right]_{xy} &= \left[\left(\vec{C} \times \hat{\vec{O}}^r\right)_x, \left(\hat{\vec{\mu}}(\vec{R}_O) \times \hat{\vec{O}}^p\right)_y\right] \\ &= \left[C_y \hat{O}^r_z - C_z \hat{O}^r_y, \hat{\mu}_z(\vec{R}_O)\hat{O}^p_x - \hat{\mu}_x(\vec{R}_O)\hat{O}^p_z\right] \\ &= \left[C_y \hat{O}^r_z, \hat{\mu}_z(\vec{R}_O)\hat{O}^p_x\right] - \left[C_y \hat{O}^r_z, \hat{\mu}_x(\vec{R}_O)\hat{O}^p_z\right] \\ &\quad - \left[C_z \hat{O}^r_y, \hat{\mu}_z(\vec{R}_O)\hat{O}^p_x\right] + \left[C_z \hat{O}^r_y, \hat{\mu}_x(\vec{R}_O)\hat{O}^p_z\right] \\ &= C_y \hat{\mu}_z(\vec{R}_O) \left[\hat{O}^r_z, \hat{O}^p_x\right] - C_y \hat{\mu}_x(\vec{R}_O) \left[\hat{O}^r_z, \hat{O}^p_z\right] \\ &\quad - C_z \hat{\mu}_z(\vec{R}_O) \left[\hat{O}^r_y, \hat{O}^p_x\right] + C_z \hat{\mu}_x(\vec{R}_O) \left[\hat{O}^r_y, \hat{O}^p_z\right] \\ &= -\imath\hbar C_y \hat{\mu}_x(\vec{R}_O) \\ &= \imath\hbar \left\{\hat{\vec{\mu}}(\vec{R}_O) \cdot \vec{C}\ \boldsymbol{I}_3 - \hat{\vec{\mu}}(\vec{R}_O) \otimes \vec{C}\right\}_{xy}\end{aligned}$$

This relation can then be used in the expression for the diamagnetic contribution to the rotational g tensor

$$\begin{aligned}g^{dia}_{J,\alpha\beta} &= \langle\Psi^{(0)}_0|\sum_i \left[(\vec{r}_i - \vec{R}_{CM}) \cdot (\vec{R}_{GO} - \vec{R}_{CM})\delta_{\alpha\beta} - (r_{i,\alpha} - R_{CM,\alpha})(R_{GO,\beta} - R_{CM,\beta})\right]|\Psi^{(0)}_0\rangle \\ &= -\langle\Psi^{(0)}_0|\left[\hat{\vec{\mu}}(\vec{R}_{CM}) \cdot (\vec{R}_{GO} - \vec{R}_{CM})\delta_{\alpha\beta} - \hat{\mu}_\alpha(\vec{R}_{CM})(R_{GO,\beta} - R_{CM,\beta})\right]|\Psi^{(0)}_0\rangle \\ &= -\frac{1}{\imath\hbar}\langle\Psi^{(0)}_0|\left[\left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \hat{\vec{O}}^r\right\}_\alpha, \left\{\hat{\vec{\mu}}(\vec{R}_{CM}) \times \hat{\vec{O}}^p\right\}_\beta\right]|\Psi^{(0)}_0\rangle \\ &= \frac{1}{\imath\hbar}\langle\Psi^{(0)}_0|\left[\left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \hat{\vec{O}}^r\right\}_\alpha, \hat{L}_\beta(\vec{R}_{CM})\right]|\Psi^{(0)}_0\rangle\end{aligned}$$

Expanding the commutator it becomes

$$g^{dia}_{J,\alpha\beta} = \frac{1}{\imath\hbar}\langle\Psi_0^{(0)}\,|\left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \hat{\vec{O}}^r\right\}_\alpha \hat{L}_\beta(\vec{R}_{CM})\,|\,\Psi_0^{(0)}\rangle$$
$$- \frac{1}{\imath\hbar}\langle\Psi_0^{(0)}\,|\,\hat{L}_\beta(\vec{R}_{CM})\left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \hat{\vec{O}}^r\right\}_\alpha |\,\Psi_0^{(0)}\rangle$$

Inserting the resolution of the identity, $\sum_n |\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}| = 1$, between the operators we get

$$g^{dia}_{J,\alpha\beta} = \frac{1}{\imath\hbar}\sum_n \langle\Psi_0^{(0)}\,|\left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \hat{\vec{O}}^r\right\}_\alpha |\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{L}_\beta(\vec{R}_{CM})\,|\,\Psi_0^{(0)}\rangle$$
$$- \frac{1}{\imath\hbar}\sum_n \langle\Psi_0^{(0)}\,|\,\hat{L}_\beta(\vec{R}_{CM})\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \hat{\vec{O}}^r\right\}_\alpha |\,\Psi_0^{(0)}\rangle$$

The constant vector $(\vec{R}_{GO} - \vec{R}_{CM})$ can temporarily be taken out of the integrals

$$g^{dia}_{J,\alpha\beta} = \frac{1}{\imath\hbar}\sum_n \left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \langle\Psi_0^{(0)}\,|\,\hat{\vec{O}}^r\,|\,\Psi_n^{(0)}\rangle\right\}_\alpha \langle\Psi_n^{(0)}\,|\,\hat{L}_\beta(\vec{R}_{CM})\,|\,\Psi_0^{(0)}\rangle$$
$$- \frac{1}{\imath\hbar}\sum_n \langle\Psi_0^{(0)}\,|\,\hat{L}_\beta(\vec{R}_{CM})\,|\,\Psi_n^{(0)}\rangle \left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \langle\Psi_n^{(0)}\,|\,\hat{\vec{O}}^r\,|\,\Psi_0^{(0)}\rangle\right\}_\alpha$$

Now the off-diagonal hypervirial relation, Eq. (3.66), can be applied leading to

$$g^{dia}_{J,\alpha\beta} = -\frac{1}{m_e}\sum_n \frac{\left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \langle\Psi_0^{(0)}\,|\,\hat{\vec{O}}^p\,|\,\Psi_n^{(0)}\rangle\right\}_\alpha \langle\Psi_n^{(0)}\,|\,\hat{L}_\beta(\vec{R}_{CM})\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}$$
$$- \frac{1}{m_e}\sum_n \frac{\langle\Psi_0^{(0)}\,|\,\hat{L}_\beta(\vec{R}_{CM})\,|\,\Psi_n^{(0)}\rangle \left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \langle\Psi_n^{(0)}\,|\,\hat{\vec{O}}^p\,|\,\Psi_0^{(0)}\rangle\right\}_\alpha}{E_0^{(0)} - E_n^{(0)}}$$

Using Eq. (3.67) and moving the constant vector $(\vec{R}_{GO} - \vec{R}_{CM})$ back in the integral completes the derivation

$$g^{dia}_{J,\alpha\beta} = -\frac{1}{m_e}\sum_{n\neq 0} \frac{\langle\Psi_0^{(0)}\,|\left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \hat{\vec{O}}^p\right\}_\alpha |\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\,\hat{L}_\beta(\vec{R}_{CM})\,|\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}$$
$$- \frac{1}{m_e}\sum_{n\neq 0} \frac{\langle\Psi_0^{(0)}\,|\,\hat{L}_\beta(\vec{R}_{CM})\,|\,\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}\,|\left\{(\vec{R}_{GO} - \vec{R}_{CM}) \times \hat{\vec{O}}^p\right\}_\alpha |\,\Psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}$$

6.4 The second-order molecular Hamiltonian reads for magnetic perturbations

$$\hat{H}^{(2)} = \sum_i^N \hat{h}^{(2)}(i)$$

with

$$\hat{h}^{(2)}(i) = \frac{e^2}{2m_e}\hat{\vec{A}}^2(\vec{r}_i)$$

The relevant vector potentials are given in Eqs. (5.55) and (6.5)

$$\hat{\vec{A}} = \hat{\vec{A}}^J + \hat{\vec{A}}^K$$

where

$$\hat{\vec{A}}^J = -\frac{m_e}{e}\boldsymbol{I}^{-1}\vec{J} \times (\vec{r} - \vec{R}_{CM})$$

$$\hat{\vec{A}}^K = \frac{\mu_0}{4\pi}\vec{m}^K \times \frac{\vec{r}_i - \vec{R}_K}{|\vec{r}_i - \vec{R}_K|^3}$$

The square of the vector potential becomes then

$$\hat{\vec{A}}^2 = \left(\hat{\vec{A}}^J\right)^2 + \left(\hat{\vec{A}}^K\right)^2 + 2\hat{\vec{A}}^J \cdot \hat{\vec{A}}^K$$

The second-order perturbation Hamiltonian for the induced contribution to the spin rotation tensor arises from the last term, which we can write as

$$\hat{h}^{(2)}(i) = \frac{e^2}{m_e}\left[-\frac{m_e}{e}\boldsymbol{I}^{-1}\vec{J} \times (\vec{r} - \vec{R}_{CM})\right] \cdot \left[\frac{\mu_0}{4\pi}\vec{m}^K \times \frac{\vec{r}_i - \vec{R}_K}{|\vec{r}_i - \vec{R}_K|^3}\right]$$

If we use again the relation

$$(\vec{A} \times \vec{B})(\vec{C} \times \vec{D}) = \vec{A}\,(\vec{D} \cdot \vec{B}\,\boldsymbol{I}_3 - \vec{D}\vec{B}^T)\,\vec{C}$$

the second-order operator becomes

$$\hat{h}^{(2)}(i) = -\frac{e\mu_0}{4\pi}\sum_{\alpha\beta} m^K_\alpha \left[(\vec{r}_i - \vec{R}_{CM}) \cdot \frac{\vec{r}_i - \vec{R}_K}{|\vec{r}_i - \vec{R}_K|^3}\delta_{\alpha\beta} - (r_{i,\alpha} - R_{CM,\alpha})\frac{r_{i,\beta} - R_{CM,\beta}}{|\vec{r}_i - \vec{R}_K|^3}\right]\left(\boldsymbol{I}^{-1}\vec{J}\right)_\beta$$

which leads to the second-order perturbation Hamiltonian for the induced contribution to the spin rotation tensor

$$\begin{aligned}\hat{H}^{(2)} &= \sum_i^N \hat{h}^{(2)}(i) \\ &= \sum_{\alpha\beta} \hat{O}^{m^K J}_{\alpha\beta}(\vec{R}_{CM}, \vec{R}_K)\; m^K_\alpha (\boldsymbol{I}^{-1}\;\vec{J})_\beta\end{aligned}$$

where

$$\hat{O}^{m^K J}_{\alpha\beta}(\vec{R}_{CM}, \vec{R}_K) = -\frac{e\mu_0}{4\pi}\sum_i \left[(\vec{r}_i - \vec{R}_{CM}) \cdot \frac{\vec{r}_i - \vec{R}_K}{\mid \vec{r}_i - \vec{R}_K \mid^3}\delta_{\alpha\beta} - (r_{i,\alpha} - R_{CM,\alpha})\frac{r_{i,\beta} - R_{K,\beta}}{\mid \vec{r}_i - \vec{R}_K \mid^3}\right]$$

6.5 Similar to Exercise 6.3 we will show the commutator relation for both a diagonal element and an off-diagonal element. Expanding therefore the xx-element we have

$$\begin{aligned}
\left[\hat{\vec{O}}^{\mu}(\vec{R}_K) \times \hat{\vec{O}}^{p}, \left(\vec{D} \times \hat{\vec{O}}^{r}\right)^T\right]_{xx} &= \left[\left(\hat{\vec{O}}^{\mu}(\vec{R}_K) \times \hat{\vec{O}}^{p}\right)_x, \left(\vec{D} \times \hat{\vec{O}}^{r}\right)_x\right] \\
&= \left[\hat{O}^{\mu}_y(\vec{R}_K)\hat{O}^p_z - \hat{O}^{\mu}_z(\vec{R}_K)\hat{O}^p_y, D_y\hat{O}^r_z - D_z\hat{O}^r_y\right] \\
&= \left[\hat{O}^{\mu}_y(\vec{R}_K)\hat{O}^p_z, D_y\hat{O}^r_z\right] - \left[\hat{O}^{\mu}_y(\vec{R}_K)\hat{O}^p_z, D_z\hat{O}^r_y\right] \\
&\quad - \left[\hat{O}^{\mu}_z(\vec{R}_K)\hat{O}^p_y, D_y\hat{O}^r_z\right] + \left[\hat{O}^{\mu}_z(\vec{R}_K)\hat{O}^p_y, D_z\hat{O}^r_y\right]
\end{aligned}$$

But the components of the $\vec{D}$ are constants and any component of $\hat{\vec{O}}^{\mu}(\vec{R}_K)$ commutes with any component of $\hat{\vec{O}}^{r}$ and we can therefore take them out of the commutator

$$\begin{aligned}
\left[\hat{\vec{O}}^{\mu}(\vec{R}_K) \times \hat{\vec{O}}^{p}, \left(\vec{D} \times \hat{\vec{O}}^{r}\right)^T\right]_{xx} &= \hat{O}^{\mu}_y(\vec{R}_K)D_y\left[\hat{O}^p_z, \hat{O}^r_z\right] - \hat{O}^{\mu}_y(\vec{R}_K)D_z\left[\hat{O}^p_z, \hat{O}^r_y\right] \\
&\quad - \hat{O}^{\mu}_z(\vec{R}_K)D_y\left[\hat{O}^p_y, \hat{O}^r_z\right] + \hat{O}^{\mu}_z(\vec{R}_K)D_z\left[\hat{O}^p_y, \hat{O}^r_y\right]
\end{aligned}$$

Evaluating the commutators $\left[\hat{O}^p_\alpha, \hat{O}^r_\beta\right] = -\imath\hbar\delta_{\alpha\beta}$ leads to

$$\begin{aligned}
\left[\hat{\vec{O}}^{\mu}(\vec{R}_K) \times \hat{\vec{O}}^{p}, \left(\vec{D} \times \hat{\vec{O}}^{r}\right)^T\right]_{xx} &= -\imath\hbar\hat{O}^{\mu}_y(\vec{R}_K)D_y - \imath\hbar\hat{O}^{\mu}_z(\vec{R}_K)D_z \\
&= \frac{\hbar}{\imath}\left\{\vec{D}\cdot\hat{\vec{O}}^{\mu}(\vec{R}_K)\ \boldsymbol{I}_3 - \vec{D}\otimes\hat{\vec{O}}^{\mu}(\vec{R}_K)\right\}_{xx}
\end{aligned}$$

For the xy-element we obtain then analogously

$$\begin{aligned}
\left[\hat{\vec{O}}^{\mu}(\vec{R}_K) \times \hat{\vec{O}}^{p}, \left(\vec{D} \times \hat{\vec{O}}^{r}\right)^T\right]_{xy} &= \left[\left(\hat{\vec{O}}^{\mu}(\vec{R}_K) \times \hat{\vec{O}}^{p}\right)_x, \left(\vec{D} \times \hat{\vec{O}}^{r}\right)_y\right] \\
&= \left[\hat{O}^{\mu}_y(\vec{R}_K)\hat{O}^p_z - \hat{O}^{\mu}_z(\vec{R}_K)\hat{O}^p_y, D_z\hat{O}^r_x - \hat{\mu}_x(\vec{R}_O)\hat{O}^r_z\right] \\
&= \left[\hat{O}^{\mu}_y(\vec{R}_K)\hat{O}^p_z, D_z\hat{O}^r_x\right] - \left[\hat{O}^{\mu}_y(\vec{R}_K)\hat{O}^p_z, D_x\hat{O}^r_z\right] \\
&\quad - \left[\hat{O}^{\mu}_z(\vec{R}_K)\hat{O}^p_y, D_z\hat{O}^r_x\right] + \left[\hat{O}^{\mu}_z(\vec{R}_K)\hat{O}^p_y, D_x\hat{O}^r_z\right] \\
&= \hat{O}^{\mu}_y(\vec{R}_K)D_z\left[\hat{O}^p_z, \hat{O}^r_x\right] - \hat{O}^{\mu}_y(\vec{R}_K)D_x\left[\hat{O}^p_z, \hat{O}^r_z\right] \\
&\quad - \hat{O}^{\mu}_z(\vec{R}_K)D_z\left[\hat{O}^p_y, \hat{O}^r_x\right] + \hat{O}^{\mu}_z(\vec{R}_K)D_x\left[\hat{O}^p_y, \hat{O}^r_z\right] \\
&= \imath\hbar\hat{O}^{\mu}_y(\vec{R}_K)D_x \\
&= -\frac{\hbar}{\imath}\left\{\vec{D}\cdot\hat{\vec{O}}^{\mu}(\vec{R}_K)\ \boldsymbol{I}_3 - \vec{D}\otimes\hat{\vec{O}}^{\mu}(\vec{R}_K)\right\}_{xy}
\end{aligned}$$

This relation can then be used in the expression for the diamagnetic contribution to the spin rotation tensor

$$
\begin{aligned}
C^{K,dia}_{\alpha\beta} &= \langle \Psi^{(0)}_0 | \sum_i^N \left[(\vec{R}_K - \vec{R}_{CM}) \cdot \frac{(\vec{r}_i - \vec{R}_K)}{| \vec{r}_i - \vec{R}_K |^3} \delta_{\alpha\beta} - (R_{K,\alpha} - R_{CM,\alpha}) \frac{(r_{i,\beta} - R_{K,\beta})}{| \vec{r}_i - \vec{R}_K |^3} \right] | \Psi^{(0)}_0 \rangle \\
&= \frac{4\pi\epsilon_0}{e} \langle \Psi^{(0)}_0 | \left[(\vec{R}_K - \vec{R}_{CM}) \cdot \hat{\vec{O}}^{\mu}(\vec{R}_K) \delta_{\alpha\beta} - (R_{K,\alpha} - R_{CM,\alpha}) \hat{O}^{\mu}_{\beta}(\vec{R}_K) \right] | \Psi^{(0)}_0 \rangle \\
&= \frac{4\pi\epsilon_0}{e} \frac{\imath}{\hbar} \langle \Psi^{(0)}_0 | \left[\left\{ \hat{\vec{O}}^{\mu}(\vec{R}_K) \times \hat{\vec{O}}^{p} \right\}_\alpha , \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \hat{\vec{O}}^{r} \right\}_\beta \right] | \Psi^{(0)}_0 \rangle \\
&= -\frac{4\pi m_e}{\mu_0 e} \frac{\imath}{\hbar} \langle \Psi^{(0)}_0 | \left[\hat{O}^{OP}_{K,\alpha}, \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \hat{\vec{O}}^{r} \right\}_\beta \right] | \Psi^{(0)}_0 \rangle
\end{aligned}
$$

Expanding the commutator it becomes

$$
\begin{aligned}
C^{K,dia}_{\alpha\beta} = &-\frac{4\pi m_e}{\mu_0 e} \frac{\imath}{\hbar} \langle \Psi^{(0)}_0 | \hat{O}^{OP}_{K,\alpha} \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \hat{\vec{O}}^{r} \right\}_\beta | \Psi^{(0)}_0 \rangle \\
&+ \frac{4\pi m_e}{\mu_0 e} \frac{\imath}{\hbar} \langle \Psi^{(0)}_0 | \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \hat{\vec{O}}^{r} \right\}_\beta \hat{O}^{OP}_{K,\alpha} | \Psi^{(0)}_0 \rangle
\end{aligned}
$$

Inserting the resolution of the identity, $\sum_n | \Psi^{(0)}_n \rangle \langle \Psi^{(0)}_n | = 1$, between the operators we get

$$
\begin{aligned}
C^{K,dia}_{\alpha\beta} = &-\frac{4\pi m_e}{\mu_0 e} \frac{\imath}{\hbar} \sum_n \langle \Psi^{(0)}_0 | \hat{O}^{OP}_{K,\alpha} | \Psi^{(0)}_n \rangle \langle \Psi^{(0)}_n | \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \hat{\vec{O}}^{r} \right\}_\beta | \Psi^{(0)}_0 \rangle \\
&+ \frac{4\pi m_e}{\mu_0 e} \frac{\imath}{\hbar} \sum_n \langle \Psi^{(0)}_0 | \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \hat{\vec{O}}^{r} \right\}_\beta | \Psi^{(0)}_n \rangle \langle \Psi^{(0)}_n | \hat{O}^{OP}_{K,\alpha} | \Psi^{(0)}_0 \rangle
\end{aligned}
$$

The constant vector $(\vec{R}_K - \vec{R}_{CM})$ can temporarily be taken out of the integrals

$$
\begin{aligned}
C^{K,dia}_{\alpha\beta} = &-\frac{4\pi m_e}{\mu_0 e} \frac{\imath}{\hbar} \sum_n \langle \Psi^{(0)}_0 | \hat{O}^{OP}_{K,\alpha} | \Psi^{(0)}_n \rangle \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \langle \Psi^{(0)}_n | \hat{\vec{O}}^{r} | \Psi^{(0)}_0 \rangle \right\}_\beta \\
&+ \frac{4\pi m_e}{\mu_0 e} \frac{\imath}{\hbar} \sum_n \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \langle \Psi^{(0)}_0 | \hat{\vec{O}}^{r} | \Psi^{(0)}_n \rangle \right\}_\beta \langle \Psi^{(0)}_n | \hat{O}^{OP}_{K,\alpha} | \Psi^{(0)}_0 \rangle
\end{aligned}
$$

Now the off-diagonal hypervirial relation, Eq. (3.66), can be applied leading to

$$
\begin{aligned}
C^{K,dia}_{\alpha\beta} = &\frac{4\pi}{\mu_0 e} \sum_n \frac{\langle \Psi^{(0)}_0 | \hat{O}^{OP}_{K,\alpha} | \Psi^{(0)}_n \rangle \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \langle \Psi^{(0)}_n | \hat{\vec{O}}^{p} | \Psi^{(0)}_0 \rangle \right\}_\beta}{E^{(0)}_0 - E^{(0)}_n} \\
&+ \frac{4\pi}{\mu_0 e} \sum_n \frac{\left\{ (\vec{R}_K - \vec{R}_{CM}) \times \langle \Psi^{(0)}_0 | \hat{\vec{O}}^{p} | \Psi^{(0)}_n \rangle \right\}_\beta \langle \Psi^{(0)}_n | \hat{O}^{OP}_{K,\alpha} | \Psi^{(0)}_0 \rangle}{E^{(0)}_0 - E^{(0)}_n}
\end{aligned}
$$

Using Eq. (3.67) and moving the constant vector $(\vec{R}_K - \vec{R}_{CM})$ back in the integral completes the derivation

$$C^{K,dia}_{\alpha\beta} = \frac{4\pi}{\mu_0 e} \sum_n \frac{\langle \Psi_0^{(0)} | \hat{O}^{OP}_{K,\alpha} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \hat{\vec{O}}^p \right\}_\beta | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}$$

$$+ \frac{4\pi}{\mu_0 e} \sum_n \frac{\langle \Psi_0^{(0)} | \left\{ (\vec{R}_K - \vec{R}_{CM}) \times \hat{\vec{O}}^p \right\}_\beta | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{O}^{OP}_{K,\alpha} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}$$

6.6 In order to derive an expression for $\hat{\hat{H}}^{(1)}$ we have to carry out the unitary transformation of the perturbed Hamiltonian in Eq. (6.60), *i.e.*

$$\hat{\hat{H}} = e^{-\imath\lambda\hat{S}} \left(\hat{H}^{(0)} + \lambda \hat{H}' \right) e^{\imath\lambda\hat{S}}$$

Expanding the exponentials and keeping terms up to first-order in λ gives

$$\begin{aligned}
\hat{\hat{H}} &= \left(1 - \imath\lambda\hat{S} + \cdots\right) \left(\hat{H}^{(0)} + \lambda\hat{H}'\right) \left(1 + \imath\lambda\hat{S} + \cdots\right) \\
&= \hat{H}^{(0)} + \lambda\hat{H}' + \imath\lambda \left[\hat{H}^{(0)}, \hat{S}\right] + \cdots \\
&= \hat{H}^{(0)} + \lambda \left(\hat{H}' + \imath \left[\hat{H}^{(0)}, \hat{S}\right]\right) + \cdots
\end{aligned}$$

The effective first-order Hamiltonian, $\hat{\hat{H}}^{(1)}$, is thus

$$\hat{\hat{H}}^{(1)} = \hat{H}' + \imath \left[\hat{H}^{(0)}, \hat{S}\right]$$

In order to determine the form of the operator $\hat{S}$ one would have to solve the equation

$$\langle \Psi_0^{(0)}(\{\vec{r}_i\}; R) | \hat{H}' + \imath \left[\hat{H}^{(0)}, \hat{S}\right] | \Psi_n^{(0)}(\{\vec{r}_i\}; R) \rangle = 0$$

which becomes

$$\begin{aligned}
&\langle \Psi_0^{(0)}(\{\vec{r}_i\}; R) | \hat{H}' | \Psi_n^{(0)}(\{\vec{r}_i\}; R) \rangle + \imath \langle \Psi_0^{(0)}(\{\vec{r}_i\}; R) | \left[\hat{H}^{(0)}, \hat{S}\right] | \Psi_n^{(0)}(\{\vec{r}_i\}; R) \rangle \\
&= \langle \Psi_0^{(0)}(\{\vec{r}_i\}; R) | \hat{H}' | \Psi_n^{(0)}(\{\vec{r}_i\}; R) \rangle \\
&\quad + \imath \left\{ E_0^{(0)}(R) \langle \Psi_0^{(0)}(\{\vec{r}_i\}; R) | \hat{S} | \Psi_n^{(0)}(\{\vec{r}_i\}; R) \rangle - \langle \Psi_0^{(0)}(\{\vec{r}_i\}; R) | \hat{S} | \Psi_n^{(0)}(\{\vec{r}_i\}; R) \rangle E_n^{(0)}(R) \right\} \\
&= 0
\end{aligned}$$

Solutions to Chapter 7

7.1 Consider the vector potential of a linearly polarized electromagnetic wave oscillating with angular frequency ω

$$\vec{A}(\vec{r},t) = \vec{\mathcal{A}}^{\omega} e^{\imath(\vec{k}\cdot\vec{r}-\omega t)} + \vec{\mathcal{A}}^{\omega *} e^{-\imath(\vec{k}\cdot\vec{r}-\omega t)}$$

The length of the wave vector $\vec{k}$ is

$$|\vec{k}| = n_r(\omega)\frac{\omega}{c} = \frac{\omega}{c}$$

where we have used that in vacuum the refractive index is $n_r(\omega) = 1$. In the Lorenz gauge, the fourth Maxwell equation, Eq. (2.129), reads

$$\nabla^2 \vec{A}(\vec{r},t) - \frac{1}{c^2}\frac{\partial^2 \vec{A}(\vec{r},t)}{\partial t^2} = 0$$

Inserting the expression for the vector potential into the fourth Maxwell equation yields

$$\begin{aligned}
&\nabla^2 \left[\vec{\mathcal{A}}^{\omega} e^{\imath(\vec{k}\cdot\vec{r}-\omega t)} + \vec{\mathcal{A}}^{\omega *} e^{-\imath(\vec{k}\cdot\vec{r}-\omega t)}\right] - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\left[\vec{\mathcal{A}}^{\omega} e^{\imath(\vec{k}\cdot\vec{r}-\omega t)} + \vec{\mathcal{A}}^{\omega *} e^{-\imath(\vec{k}\cdot\vec{r}-\omega t)}\right] \\
&= \left(\frac{\partial^2}{\partial r_x^2} + \frac{\partial^2}{\partial r_y^2} + \frac{\partial^2}{\partial r_z^2}\right)\left[\vec{\mathcal{A}}^{\omega} e^{\imath(\vec{k}\cdot\vec{r}-\omega t)} + \vec{\mathcal{A}}^{\omega *} e^{-\imath(\vec{k}\cdot\vec{r}-\omega t)}\right] \\
&\quad - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\left[\vec{\mathcal{A}}^{\omega} e^{\imath(\vec{k}\cdot\vec{r}-\omega t)} + \vec{\mathcal{A}}^{\omega *} e^{-\imath(\vec{k}\cdot\vec{r}-\omega t)}\right] \\
&= \left[(\imath k_x)^2 + (\imath k_y)^2 + (\imath k_z)^2\right]\vec{\mathcal{A}}^{\omega} e^{\imath(\vec{k}\cdot\vec{r}-\omega t)} + \left[(-\imath k_x)^2 + (-\imath k_y)^2 + (-\imath k_z)^2\right]\vec{\mathcal{A}}^{\omega *} e^{-\imath(\vec{k}\cdot\vec{r}-\omega t)} \\
&\quad - \frac{(-\imath\omega)^2}{c^2}\vec{\mathcal{A}}^{\omega} e^{\imath(\vec{k}\cdot\vec{r}-\omega t)} - \frac{(\imath\omega)^2}{c^2}\vec{\mathcal{A}}^{\omega *} e^{-\imath(\vec{k}\cdot\vec{r}-\omega t)} \\
&= -|\vec{k}|^2\left[\vec{\mathcal{A}}^{\omega} e^{\imath(\vec{k}\cdot\vec{r}-\omega t)} + \vec{\mathcal{A}}^{\omega *} e^{-\imath(\vec{k}\cdot\vec{r}-\omega t)}\right] + \frac{\omega^2}{c^2}\left[\vec{\mathcal{A}}^{\omega} e^{\imath(\vec{k}\cdot\vec{r}-\omega t)} + \vec{\mathcal{A}}^{\omega *} e^{-\imath(\vec{k}\cdot\vec{r}-\omega t)}\right] \\
&= -|\vec{k}|^2\vec{A}(\vec{r},t) + \frac{\omega^2}{c^2}\vec{A}(\vec{r},t) = \left(-|\vec{k}|^2 + \frac{\omega^2}{c^2}\right)\vec{A}(\vec{r},t) = \left(-\frac{\omega^2}{c^2} + \frac{\omega^2}{c^2}\right)\vec{A}(\vec{r},t) = 0
\end{aligned}$$

showing that the vector potential is indeed a solution to the fourth Maxwell equation.

7.2 The oscillator strength in the mixed representation is given by

$$f_{n0}^{m} = -\frac{2}{3}\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\hat{\vec{O}}^{p}|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{\vec{O}}^{r}|\Psi_0^{(0)}\rangle$$

This can be rewritten according to

$$\begin{aligned}
f_{n0}^{m} &= -\frac{2}{3}\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\hat{\vec{O}}^r|\Psi_n^{(0)}\rangle^*\langle\Psi_n^{(0)}|\hat{\vec{O}}^p|\Psi_0^{(0)}\rangle^* \\
&= -\frac{2}{3}\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\hat{\vec{O}}^r|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\left(-\hat{\vec{O}}^p\right)|\Psi_0^{(0)}\rangle \\
&= \frac{2}{3}\frac{1}{\imath\hbar}\langle\Psi_0^{(0)}|\hat{\vec{O}}^r|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{\vec{O}}^p|\Psi_0^{(0)}\rangle
\end{aligned}$$

where we have assumed real wavefunctions and used that the momentum operator is purely imaginary. If we combine now the two formulations, we obtain a third alternative expression for the mixed representation of the oscillator strength

$$f_{n0}^{m} = \frac{1}{3}\frac{1}{\imath\hbar}\left(\langle\Psi_0^{(0)}|\hat{\vec{O}}^r|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{\vec{O}}^p|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|\hat{\vec{O}}^p|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{\vec{O}}^r|\Psi_0^{(0)}\rangle\right)$$

which will be useful in the subsequent derivation.

The dipole oscillator strength sum $S(0)$ is given by

$$S(0) = \sum_{n\neq 0}(E_n^{(0)} - E_0^{(0)})^0 f_{n0}^{m} = \sum_{n\neq 0} f_{n0}^{m}$$

where we can include $n = 0$ in the summation, as the term is anyway zero. Inserting the expression for the oscillator strength gives

$$S(0) = \frac{1}{3}\frac{1}{\imath\hbar}\sum_{n}\left(\langle\Psi_0^{(0)}|\hat{\vec{O}}^r|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{\vec{O}}^p|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|\hat{\vec{O}}^p|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{\vec{O}}^r|\Psi_0^{(0)}\rangle\right)$$

or in terms of the cartesian components

$$S(0) = \frac{1}{3}\frac{1}{\imath\hbar}\sum_{n}\sum_{\alpha=x,y,z}\left(\langle\Psi_0^{(0)}|\hat{O}_\alpha^r|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}_\alpha^p|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|\hat{O}_\alpha^p|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}_\alpha^r|\Psi_0^{(0)}\rangle\right)$$

Now we make use of the resolution of the identity

$$\begin{aligned}
S(0) &= \frac{1}{3}\frac{1}{\imath\hbar}\sum_{\alpha=x,y,z}\left(\langle\Psi_0^{(0)}|\hat{O}_\alpha^r\hat{O}_\alpha^p|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|\hat{O}_\alpha^p\hat{O}_\alpha^r|\Psi_0^{(0)}\rangle\right) \\
&= \frac{1}{3}\frac{1}{\imath\hbar}\sum_{\alpha=x,y,z}\langle\Psi_0^{(0)}|[\hat{O}_\alpha^r,\hat{O}_\alpha^p]|\Psi_0^{(0)}\rangle
\end{aligned}$$

Evaluating the commutator according to

$$\langle\Psi_0^{(0)}|[\hat{O}_\alpha^r,\hat{O}_\beta^p]|\Psi_0^{(0)}\rangle = \imath\hbar N\delta_{\alpha\beta}$$

gives the Thomas-Reiche-Kuhn sum rule

$$S(0) = \frac{1}{3}\frac{1}{\imath\hbar}\sum_{\alpha=x,y,z}\imath\hbar N = N$$

7.3 The positive even dipole oscillator strength sums can be obtained as derivatives of the frequency-dependent polarizability as

$$S^l_{\alpha\beta}(2k) = (-1)^{k-1}\frac{m_e}{e^2\hbar^2}\frac{\hbar^{2k}}{2^k k!}\lim_{\omega\to\infty}\left(\omega^3\frac{d}{d\omega}\right)^k \hbar^2\omega^2\alpha_{\alpha\beta}(-\omega;\omega)$$

for $k = 0, 1, 2, \cdots$. The frequency-dependent polarizability reads

$$\alpha_{\alpha\beta}(-\omega;\omega) = \frac{\hbar^2 e^2}{m_e}\sum_{n\neq 0}\frac{f^l_{n0,\alpha\beta}}{(E^{(0)}_n - E^{(0)}_0)^2 - \hbar^2\omega^2}$$

From this alternative expression for the dipole oscillator strength sum, we will derive the Thomas-Reiche-Kuhn sum rule, i.e. $S(0) = N$. For $k = 0$ the general expression becomes

$$\begin{aligned}
S^l_{\alpha\beta}(0) &= -\frac{m_e}{e^2\hbar^2}\lim_{\omega\to\infty}\hbar^2\omega^2\alpha_{\alpha\beta}(-\omega;\omega)\\
&= -\lim_{\omega\to\infty}\hbar^2\omega^2\sum_{n\neq 0}\frac{f^l_{n0,\alpha\beta}}{(E^{(0)}_n - E^{(0)}_0)^2 - \hbar^2\omega^2}\\
&= -\lim_{\omega\to\infty}\sum_{n\neq 0}\frac{f^l_{n0,\alpha\beta}}{\left(\frac{E^{(0)}_n - E^{(0)}_0}{\hbar\omega}\right)^2 - 1}\\
&= \sum_{n\neq 0} f^l_{n0,\alpha\beta}
\end{aligned}$$

Averaging of the diagonal elements of the oscillator strengths gives then

$$S(0) = \frac{1}{3}\sum_{\alpha=x,y,z} S^l_{\alpha\alpha}(0) = \frac{1}{3}\sum_{\alpha=x,y,z}\sum_{n\neq 0} f^l_{n0,\alpha\alpha} = \sum_{n\neq 0}\frac{1}{3}\sum_{\alpha=x,y,z} f^l_{n0,\alpha\alpha} = \sum_{n\neq 0} f^l_{n0}$$

For the $S^l(2)$ sum we consider now $k = 1$ in the general expression

$$S^l_{\alpha\beta}(2) = \frac{m_e}{e^2\hbar^2}\frac{\hbar^2}{2}\lim_{\omega\to\infty}\left(\omega^3\frac{d}{d\omega}\right)\hbar^2\omega^2\alpha_{\alpha\beta}(-\omega;\omega)$$

First, we take the derivative

$$\begin{aligned}
\frac{d}{d\omega}\left[\hbar^2\omega^2\alpha_{\alpha\beta}(-\omega;\omega)\right] &= \frac{d}{d\omega}\left[\hbar^2\omega^2\frac{e^2\hbar^2}{m_e}\sum_{n\neq 0}\frac{f^l_{n0,\alpha\beta}}{(E^{(0)}_n - E^{(0)}_0)^2 - \hbar^2\omega^2}\right]\\
&= \frac{e^2\hbar^2}{m_e}\sum_{n\neq 0} f^l_{n0,\alpha\beta}\frac{d}{d\omega}\frac{1}{\left(\frac{E^{(0)}_n - E^{(0)}_0}{\hbar\omega}\right)^2 - 1}
\end{aligned}$$

which gives

$$\frac{d}{d\omega}\left[\hbar^2\omega^2\alpha_{\alpha\beta}(-\omega;\omega)\right]$$

$$= \frac{e^2\hbar^2}{m_e}\sum_{n\neq 0} f^l_{n0,\alpha\beta}\left\{-\left[\left(\frac{E_n^{(0)}-E_0^{(0)}}{\hbar\omega}\right)^2 - 1\right]^{-2}\left(\frac{E_n^{(0)}-E_0^{(0)}}{\hbar}\right)^2(-2\omega^{-3})\right\}$$

$$= \frac{e^2}{m_e}\frac{2}{\omega^3}\sum_{n\neq 0} f^l_{n0,\alpha\beta}\frac{\left(E_n^{(0)}-E_0^{(0)}\right)^2}{\left[\left(\frac{E_n^{(0)}-E_0^{(0)}}{\hbar\omega}\right)^2 - 1\right]^2}$$

Inserting this into the expression for $S^l_{\alpha\beta}(2)$ yields

$$S^l_{\alpha\beta}(2) = \frac{m_e}{e^2\hbar^2}\frac{\hbar^2}{2}\frac{2e^2}{m_e}\sum_{n\neq 0} f^l_{n0,\alpha\beta}\left(E_n^{(0)}-E_0^{(0)}\right)^2 \lim_{\omega\to\infty}\frac{1}{\left[\left(\frac{E_n^{(0)}-E_0^{(0)}}{\hbar\omega}\right)^2 - 1\right]^2}$$

$$= \sum_{n\neq 0} f^l_{n0,\alpha\beta}\left(E_n^{(0)}-E_0^{(0)}\right)^2$$

Finally, we take the average of the diagonal elements on both sides of the equality

$$S^l(2) = \frac{1}{3}\sum_{\alpha=x,y,z} S^l_{\alpha\alpha}(2) = \sum_{n\neq 0}(E_n^{(0)}-E_0^{(0)})^2\frac{1}{3}\sum_{\alpha=x,y,z} f^l_{n0,\alpha\beta}$$

$$= \sum_{n\neq 0}\left(E_n^{(0)}-E_0^{(0)}\right)^2 f^l_{n0},$$

which is identical to the definition in Eq. (7.79) for $k = 2$.

Solutions to Chapter 8

8.1 We remember that we only need to consider functions of the type:

$$\Theta^{(0,0)}_{v_b=1}(\{Q_a\}) = \vartheta_{v_b=1}(Q_b)\prod_{a\neq b}\vartheta_{v_a=0}(Q_a)$$

The only non-zero matrix elements between two harmonic oscillator functions $\vartheta_{v_a}, \vartheta_{v'_a}$ and Q_a to power of up to three, when v_a and v'_a are equal or differ by 1 are:

$$\begin{aligned}
\langle\vartheta_{v_a}|Q_a|\vartheta_{v_a+1}\rangle &= \sqrt{\frac{\hbar}{2\omega_a}(v_a+1)}\\
\langle\vartheta_{v_a}|Q_a^2|\vartheta_{v_a}\rangle &= \frac{\hbar}{\omega_a}(v_a+\tfrac{1}{2})\\
\langle\vartheta_{v_a}|Q_a^3|\vartheta_{v_a+1}\rangle &= 3\left[\frac{\hbar}{2\omega_a}(v_a+1)\right]^{\frac{3}{2}}
\end{aligned}$$

We see therefore that $\langle\Theta^{(0,0)}_{v_b=1}(\{Q_a\})\,|Q_cQ_dQ_e|\Theta^{(0,0)}_{v=0}(\{Q_a\})\rangle$ is only non-zero when either all the indexes b,c,d,e are the same, or when b is equal to one of c,d,e and the other two are the same but different from b. Inserting the above expressions we get

$$\begin{aligned}
&\frac{1}{6}\sum_{cde}K_{cde}\langle\Theta^{(0,0)}_{v_b=1}(\{Q_a\})\,|Q_cQ_dQ_e|\Theta^{(0,0)}_{v=0}(\{Q_a\})\rangle\\
&= \frac{1}{6}K_{bbb}\langle\vartheta_{v_b=1}|Q_a^3|\vartheta_{v_b=0}\rangle + \frac{1}{2}\sum_{c\neq b}K_{bcc}\langle\vartheta_{v_b=1}|Q_b|\vartheta_{v_b=0}\rangle\langle\vartheta_{v_c}|Q_c^2|\vartheta_{v_c}\rangle\\
&= \frac{1}{2}K_{bbb}\left(\frac{\hbar}{2\omega_b}\right)^{\frac{3}{2}} + \frac{1}{2}\sqrt{\frac{\hbar}{2\omega_b}}\sum_{c\neq b}K_{bcc}\frac{\hbar}{2\omega_c}\\
&= \frac{\hbar}{4}\sqrt{\frac{\hbar}{2\omega_b}}\sum_{c}\frac{K_{bcc}}{\omega_c}
\end{aligned}$$

8.2 In order to derive the expression for the first order correction, we need to calculate both integrals in equation (8.43) to the appropriate order. In the first integral we have

$$\langle\Theta^{(0)}_{v=0}|Q_a|\Theta^{(0)}_{v=0}\rangle^{(1)} = \langle\Theta^{(0,0)}_{v=0}|Q_a|\Theta^{(0,1)}_{v=0}\rangle + \langle\Theta^{(0,1)}_{v=0}|Q_a|\Theta^{(0,0)}_{v=0}\rangle = 2\langle\Theta^{(0,0)}_{v=0}|Q_a|\Theta^{(0,1)}_{v=0}\rangle$$

remembering that the zeroth-order term $\langle\Theta^{(0)}_{v=0}|Q_a|\Theta^{(0)}_{v=0}\rangle = \langle\vartheta_{v_a}|Q_a|\vartheta_{v_a}\rangle$ vanishes. Inserting the expression for the first-order correction in equation (8.42) we have:

$$
\begin{aligned}
2\langle\Theta_{v=0}^{(0,0)}|Q_a|\Theta_{v=0}^{(0,1)}\rangle &= -\frac{1}{4}\sum_b 2\langle\Theta_{v=0}^{(0,0)}|Q_a|\Theta_{v_b=1}^{(0,0)}\rangle\sqrt{\frac{\hbar}{2\omega_b^3}}\sum_c\frac{K_{bcc}}{\omega_c} \\
&= -\frac{1}{4}\sum_b 2\delta_{ab}\langle\vartheta_{v_a=0}|Q_a|\vartheta_{v_a=1}\rangle\sqrt{\frac{\hbar}{2\omega_b^3}}\sum_c\frac{K_{bcc}}{\omega_c} \\
&= -\frac{1}{2}\sqrt{\frac{\hbar}{2\omega_a}}\sqrt{\frac{\hbar}{2\omega_a^3}}\sum_c\frac{K_{acc}}{\omega_c} = -\frac{\hbar}{4\omega_a^2}\sum_c\frac{K_{acc}}{\omega_c}
\end{aligned}
$$

For the second integral we have:

$$
\langle\Theta_{v=0}^{(0,0)}|Q_aQ_b|\Theta_{v=0}^{(0,0)}\rangle = \delta_{ab}\langle\vartheta_{v_a}|Q_a^2|\vartheta_{v_a}\rangle = \delta_{ab}\frac{\hbar}{2\omega_a}
$$

Inserting this in (8.43) we obtain the wanted expression for the vibrational correction:

$$
\Delta\alpha_{\alpha\beta}^{ZPVC} = -\frac{\hbar}{4}\sum_a\frac{1}{\omega_a^2}\left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_a}\right)_{\mathbf{Q=0}}\sum_c\left(\frac{K_{acc}}{\omega_c}\right) + \frac{\hbar}{4}\sum_a\frac{1}{\omega_a}\left(\frac{\partial^2\alpha_{\alpha\beta}}{\partial Q_a^2}\right)_{\mathbf{Q=0}}
$$

Solutions to Chapter 9

9.1 In Møller-Plesset perturbation theory the total field-free Hamiltonian is partitioned as:

$$\hat{H}^{(0)} = \hat{F} + \hat{V}$$

where the fluctuation potential, $\hat{V}$, is treated as perturbation. The unperturbed wavefunctions are the eigenfunctions of the Fock operator, $\hat{F}$, which we know to be Slater determinants formed from the Hartree-Fock molecular orbitals. The Slater determinant with the lowest energy is the SCF wavefunction. The zeroth- and first-order energies can thus be expressed using Rayleigh-Schrödinger perturbation theory according to Eq. (3.14) and Eq. (3.29) as

$$E^{MP0} = \langle \Phi_0^{SCF} | \hat{F} | \Phi_0^{SCF} \rangle$$
$$E^{MP1} = \langle \Phi_0^{SCF} | \hat{V} | \Phi_0^{SCF} \rangle$$

The sum of the zero- and first-order energies is:

$$E^{MP0} + E^{MP1} = \langle \Phi_0^{SCF} | \hat{F} + \hat{V} | \Phi_0^{SCF} \rangle = \langle \Phi_0^{SCF} | \hat{H}^{(0)} | \Phi_0^{SCF} \rangle = E^{SCF}$$

which is the Hartree-Fock energy as it is defined as the expectation value of the SCF wavefunction over the total Hamiltonian.

9.2 To determine which determinants can contribute to the first order Møller-Plesset wavefunction, we need to consider the transition element

$$\langle \Phi_n | \hat{V} | \Phi_0^{SCF} \rangle$$

which is the only term in (9.66) that can be zero. Since

$$\hat{V} = \sum_{i<j} \hat{g}(i,j) - \sum_i \hat{v}^{HF}(i)$$

is a two electron operator, the transition element must be zero by the Slater-Condon rules if $|\Phi_n\rangle$ differs from $|\Phi_0^{SCF}\rangle$ in more than two spin-orbitals. That single excited determinants cannot contribute, can be shown most easily by noting that

$$\hat{V} = \hat{H}^{(0)} - \hat{F}$$

An element with a singly excited determinant is then

$$\langle \Phi_i^a | \hat{V} | \Phi_0^{SCF} \rangle = \langle \Phi_i^a | \hat{H}^{(0)} | \Phi_0^{SCF} \rangle - \langle \Phi_i^a | \hat{F} | \Phi_0^{SCF} \rangle$$

Both of the elements on the right can be seen to be zero by using the Brillouin theorem, Eq. (9.61), that is they both evaluate to $\langle \psi_a | \hat{f} | \psi_i \rangle = 0$. Thus only double excited determinants can contribute to the MP first order correction to the wavefunction.

9.3 We have the coupled cluster "Λ"-state:

$$\langle \Phi_0^{\Lambda}| = \langle \Phi_0^{SCF}|(1+\hat{\Lambda})e^{-\hat{T}}$$

where the $\hat{\Lambda}$ operator is defined as a linear combination of all de-excitation operators as in Eq. (9.35) - Eq. (9.38). We use here the general form:

$$\hat{\Lambda} = \sum_{i_\mu} \lambda_{i_\mu} {}^{d}h_{i_\mu}$$

Explicitly inserting this in the asymmetric expectation value, Eq. (9.95), gives

$$\begin{aligned} E_0^{CC,\Lambda} &= \langle \Phi_0^{SCF}|(1+\hat{\Lambda})e^{-\hat{T}}\hat{H}^{(0)}e^{\hat{T}}|\Phi_0^{SCF}\rangle \\ &= \langle \Phi_0^{SCF}|e^{-\hat{T}}\hat{H}^{(0)}e^{\hat{T}}|\Phi_0^{SCF}\rangle + \sum_{i_\mu} \lambda_{i_\mu} \langle \Phi_0^{SCF}|{}^{d}h_{i_\mu} e^{-\hat{T}}\hat{H}^{(0)}e^{\hat{T}}|\Phi_0^{SCF}\rangle \end{aligned}$$

The first term on the right can easily be identified as the coupled cluster energy. Remembering that the coupled cluster vector function, Eq. (9.81), is defined as

$$e_{i_\mu} = \langle \Phi_0^{SCF}|{}^{d}h_{i_\mu} e^{-\hat{T}}\hat{H}^{(0)}|\Phi_0^{CC}\rangle$$

The asymmetric expectation value reduces to

$$E_0^{CC,\Lambda} = E_0^{CC} + \sum_{i_\mu} \lambda_{i_\mu} e_{i_\mu} = L_0^{CC}$$

which is, what we wanted to show.

Solutions to Chapter 10

10.1 Since the operator $\hat{O}$ is a sum of one-electron operators $\hat{o}$, the Slater-Condon rules in Eq. (9.58) lead directly to

$$\langle \Phi_0^{SCF}|\hat{O}|\Phi_i^a\rangle = \langle \psi_a|\hat{o}|\psi_i\rangle$$

Similarly the matrix elements over the Hartree-Fock Hamiltonian, Eq. (9.15), gives a sum over one electron integrals of the Fock operator, which using the expression for the orbital energy, Eq. (9.17), are seen to be

$$\langle \Phi_0^{SCF}|\hat{F}|\Phi_0^{SCF}\rangle = \sum_j^N \langle \psi_j|\hat{f}|\psi_j\rangle = \sum_j^N \epsilon_j$$

$$\langle \Phi_i^a|\hat{F}|\Phi_i^a\rangle = \sum_{j\neq i} \epsilon_j + \epsilon_a$$

And so we obtain

$$\langle \Phi_i^a|\hat{F}|\Phi_i^a\rangle - \langle \Phi_0^{SCF}|\hat{F}|\Phi_0^{SCF}\rangle = \epsilon_a - \epsilon_i$$

10.2 We can show that a matrix is the inverse of another matrix by showing that their product gives a unit matrix. To show Eq. (10.14) we thus evaluate:

$$\begin{pmatrix} \mathbf{U} & \mathbf{V} \\ \mathbf{W} & \mathbf{Z} \end{pmatrix} \begin{pmatrix} \left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)^{-1} & -\mathbf{U}^{-1}\mathbf{V}\left(\mathbf{Z} - \mathbf{W}\mathbf{U}^{-1}\mathbf{V}\right)^{-1} \\ -\mathbf{Z}^{-1}\mathbf{W}\left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)^{-1} & \left(\mathbf{Z} - \mathbf{W}\mathbf{U}^{-1}\mathbf{V}\right)^{-1} \end{pmatrix} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix}$$

where

$$\begin{aligned}
\mathbf{A} &= \mathbf{U}\left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)^{-1} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)^{-1} \\
&= \left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)\left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)^{-1} = \mathbf{I} \\
\mathbf{B} &= -\mathbf{U}\mathbf{U}^{-1}\mathbf{V}\left(\mathbf{Z} - \mathbf{W}\mathbf{U}^{-1}\mathbf{V}\right)^{-1} + \mathbf{V}\left(\mathbf{Z} - \mathbf{W}\mathbf{U}^{-1}\mathbf{V}\right)^{-1} = \mathbf{0} \\
\mathbf{C} &= \mathbf{W}\left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)^{-1} - \mathbf{Z}\mathbf{Z}^{-1}\mathbf{W}\left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)^{-1} = \mathbf{0} \\
\mathbf{D} &= -\mathbf{W}\mathbf{U}^{-1}\mathbf{V}\left(\mathbf{Z} - \mathbf{W}\mathbf{U}^{-1}\mathbf{V}\right)^{-1} + \mathbf{Z}\left(\mathbf{Z} - \mathbf{W}\mathbf{U}^{-1}\mathbf{V}\right)^{-1} \\
&= \left(-\mathbf{W}\mathbf{U}^{-1}\mathbf{V} + \mathbf{Z}\right)\left(\mathbf{Z} - \mathbf{W}\mathbf{U}^{-1}\mathbf{V}\right)^{-1} = \mathbf{I}
\end{aligned}$$

where the matrices $\mathbf{I}$ and $\mathbf{0}$ are appropriately sized unit and zero matrices, respectively. W obtain therefore

$$\begin{pmatrix} \mathbf{U} & \mathbf{V} \\ \mathbf{W} & \mathbf{Z} \end{pmatrix} \begin{pmatrix} \left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)^{-1} & -\mathbf{U}^{-1}\mathbf{V}\left(\mathbf{Z} - \mathbf{W}\mathbf{U}^{-1}\mathbf{V}\right)^{-1} \\ -\mathbf{Z}^{-1}\mathbf{W}\left(\mathbf{U} - \mathbf{V}\mathbf{Z}^{-1}\mathbf{W}\right)^{-1} & \left(\mathbf{Z} - \mathbf{W}\mathbf{U}^{-1}\mathbf{V}\right)^{-1} \end{pmatrix} = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix}$$

showing that it is indeed the inverse.

Another way to show Eq. (10.14) is to derive the inverse. We recall therefore that the solution of a set of linear equations

$$\mathbf{M}\begin{pmatrix}\mathbf{x}\\ \mathbf{y}\end{pmatrix} = \begin{pmatrix}\mathbf{U} & \mathbf{V}\\ \mathbf{W} & \mathbf{Z}\end{pmatrix}\begin{pmatrix}\mathbf{x}\\ \mathbf{y}\end{pmatrix} = \begin{pmatrix}\mathbf{c}\\ \mathbf{d}\end{pmatrix}$$

is given by

$$\begin{pmatrix}\mathbf{x}\\ \mathbf{y}\end{pmatrix} = \begin{pmatrix}\mathbf{U} & \mathbf{V}\\ \mathbf{W} & \mathbf{Z}\end{pmatrix}^{-1}\begin{pmatrix}\mathbf{c}\\ \mathbf{d}\end{pmatrix}$$

This implies that the inverse of $\begin{pmatrix}\mathbf{U} & \mathbf{V}\\ \mathbf{W} & \mathbf{Z}\end{pmatrix}$ can be obtained by solving the following linear equations.

$$\begin{aligned}\mathbf{Ux} + \mathbf{Vy} &= \mathbf{c}\\ \mathbf{Wx} + \mathbf{Zy} &= \mathbf{d}\end{aligned}$$

Assuming that $\mathbf{Z}$ is non-singular we obtain from the second equation for $\mathbf{y}$

$$\mathbf{y} = \mathbf{Z}^{-1}(\mathbf{d} - \mathbf{Wx})$$

and then from the first equation for $\mathbf{x}$

$$\mathbf{x} = \left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)^{-1}\left(\mathbf{c} - \mathbf{VZ}^{-1}\mathbf{d}\right)$$

This means that

$$\begin{pmatrix}\mathbf{x}\\ \mathbf{y}\end{pmatrix} = \begin{pmatrix}\left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)^{-1} & -\left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)^{-1}\mathbf{VZ}^{-1}\\ -\mathbf{Z}^{-1}\mathbf{W}\left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)^{-1} & \mathbf{Z}^{-1} + \mathbf{Z}^{-1}\mathbf{W}\left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)^{-1}\mathbf{VZ}^{-1}\end{pmatrix}\begin{pmatrix}\mathbf{c}\\ \mathbf{d}\end{pmatrix}$$

Finally $\left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)^{-1}\mathbf{VZ}^{-1}$ can be rewritten using the usual rules concerning the inverse of a product of matrices

$$\begin{aligned}\left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)^{-1}\mathbf{VZ}^{-1} &= \left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)^{-1}\left(\mathbf{ZV}^{-1}\right)^{-1}\\ &= \left[\left(\mathbf{ZV}^{-1}\right)\left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)\right]^{-1}\\ &= \left(\mathbf{ZV}^{-1}\mathbf{U} - \mathbf{W}\right)^{-1}\end{aligned}$$

and for the $\mathbf{M}_{2,2}$ element the Woodbury matrix identity can be used giving

$$\mathbf{Z}^{-1} + \mathbf{Z}^{-1}\mathbf{W}\left(\mathbf{U} - \mathbf{VZ^{-1}W}\right)^{-1}\mathbf{VZ}^{-1} = \left(\mathbf{Z} - \mathbf{WU}^{-1}\mathbf{V}\right)^{-1}$$

10.3 The matrix form of the polarization propagator is given as

$$\langle\langle \hat{P}_\alpha; \hat{O}^\omega_{\beta\ldots}\rangle\rangle = \left(\mathbf{T}_1^T(\hat{P}_\alpha)\ ,\ \mathbf{T}_{2\ldots}^T(\hat{P}_\alpha)\right)\begin{pmatrix}\mathbf{M}_{11} & \mathbf{M}_{12\ldots}\\ \mathbf{M}_{2\ldots1} & \mathbf{M}_{2\ldots2\ldots}\end{pmatrix}^{-1}\begin{pmatrix}\mathbf{T}_1(\hat{O}^\omega_{\beta\ldots})\\ \mathbf{T}_{2\ldots}(\hat{O}^\omega_{\beta\ldots})\end{pmatrix}$$

According to Eq. (10.14) or the solution to exercise 10.2 the inverse of the principal propagator can be rewritten as

$$\begin{pmatrix} \mathbf{M}_{11} & \mathbf{M}_{12\cdots} \\ \mathbf{M}_{2\cdots 1} & \mathbf{M}_{2\cdots 2\cdots} \end{pmatrix}^{-1}$$
$$= \begin{pmatrix} \mathbf{P}^{-1} & -\mathbf{P}^{-1}\mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots} \\ -\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}\mathbf{P}^{-1} & \mathbf{M}^{-1}_{2\cdots 2\cdots} + \mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}\mathbf{P}^{-1}\mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots} \end{pmatrix}$$

where

$$\mathbf{P}^{-1} = \left(\mathbf{M}_{11} - \mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}\right)^{-1}$$

Inserting this in the expression for the polarization propagator gives

$$\langle\langle \hat{P}_\alpha; \hat{O}^\omega_{\beta\cdots}\rangle\rangle = \left(\mathbf{T}^T_1(\hat{P}_\alpha)\ ,\ \mathbf{T}^T_{2\cdots}(\hat{P}_\alpha)\right)$$
$$\begin{pmatrix} \mathbf{P}^{-1} & -\mathbf{P}^{-1}\mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots} \\ -\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}\mathbf{P}^{-1} & \mathbf{M}^{-1}_{2\cdots 2\cdots} + \mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}\mathbf{P}^{-1}\mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots} \end{pmatrix} \begin{pmatrix} \mathbf{T}_1(\hat{O}^\omega_{\beta\cdots}) \\ \mathbf{T}_{2\cdots}(\hat{O}^\omega_{\beta\cdots}) \end{pmatrix}$$

Carrying out the matrix times vector multiplications gives

$$\langle\langle \hat{P}_\alpha; \hat{O}^\omega_{\beta\cdots}\rangle\rangle = \left(\mathbf{T}^T_1(\hat{P}_\alpha)\ ,\ \mathbf{T}^T_{2\cdots}(\hat{P}_\alpha)\right)$$
$$\begin{pmatrix} \mathbf{P}^{-1}\left[\mathbf{T}_1(\hat{O}^\omega_{\beta\cdots}) - \mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{T}_{2\cdots}(\hat{O}^\omega_{\beta\cdots})\right] \\ -\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}\mathbf{P}^{-1}\left[\mathbf{T}_1(\hat{O}^\omega_{\beta\cdots}) - \mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{T}_{2\cdots}(\hat{O}^\omega_{\beta\cdots})\right] + \mathbf{M}^{-1}_{2\cdots 2}\mathbf{T}_{2\cdots}(\hat{O}^\omega_{\beta\cdots}) \end{pmatrix}$$

Combining these results, we can write the partitioned form of the propagator as

$$\langle\langle \hat{P}_\alpha; \hat{O}^\omega_{\beta\cdots}\rangle\rangle$$
$$= \left[\mathbf{T}^T_1(\hat{P}_\alpha) - \mathbf{T}^T_{2\cdots}(\hat{P}_\alpha)\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}\right]\mathbf{P}^{-1}\left[\mathbf{T}_1(\hat{O}^\omega_{\beta\cdots}) - \mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{T}_{2\cdots}(\hat{O}^\omega_{\beta\cdots})\right]$$
$$+ \mathbf{T}^T_{2\cdots}(\hat{P}_\alpha)\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{T}_{2\cdots}(\hat{O}^\omega_{\beta\cdots})$$

Or if we insert the expression for $\mathbf{P} = \mathbf{M}_{11} - \mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}$ again

$$\langle\langle \hat{P}_\alpha; \hat{O}^\omega_{\beta\cdots}\rangle\rangle = \left[\mathbf{T}^T_1(\hat{P}_\alpha) - \mathbf{T}^T_{2\cdots}(\hat{P}_\alpha)\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}\right]$$
$$\times\left(\mathbf{M}_{11} - \mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{M}_{2\cdots 1}\right)^{-1}\left[\mathbf{T}_1(\hat{O}^\omega_{\beta\cdots}) - \mathbf{M}_{12\cdots}\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{T}_{2\cdots}(\hat{O}^\omega_{\beta\cdots})\right]$$
$$+ \mathbf{T}^T_{2\cdots}(\hat{P}_\alpha)\mathbf{M}^{-1}_{2\cdots 2\cdots}\mathbf{T}_{2\cdots}(\hat{O}^\omega_{\beta\cdots})$$

10.4 We need to shown that

$$^{e}P^{(1)}_{\alpha,ai} = \langle\Phi^{\mathrm{MP}}|[\hat{P}_\alpha, \hat{q}^\dagger_{ai}]|\Phi^{\mathrm{MP}}\rangle^{(1)} = 0$$

Evaluating the matrix element to first order means that we have to replace one of the wavefunctions with the SCF wavefunction and the other with the MP1 correction to the wavefunction, Eq. (9.66),

$$|\Phi^{\mathrm{MP1}}\rangle = \sum_{j<k}\sum_{b<c} t_{jk}^{bc}|\Phi_{jk}^{bc}\rangle$$

It is easy to see, that this integral is zero, when we the bra is the SCF wavefunction and the ket the MP1 correction. The commutator gives two terms and in one we have $\hat{q}_{ai}^{\dagger}$ acting on a SCF function to the left, which gives zero, and in the other $\hat{q}_{ai}^{\dagger}$ acts to the right on the MP1 wavefunction, which gives a triply exited state and makes the integral vanish due to the Slater-Condon rules. We therefore need consider only elements of the type:

$$\langle\Phi_{jk}^{bc}|[\hat{P}_\alpha, \hat{q}_{ai}^{\dagger}]|\Phi_0^{SCF}\rangle = \langle\Phi_{jk}^{bc}|\hat{P}_\alpha\hat{q}_{ai}^{\dagger}|\Phi_0^{SCF}\rangle - \langle\Phi_{jk}^{bc}|\hat{q}_{ai}^{\dagger}\hat{P}_\alpha|\Phi_0^{SCF}\rangle$$

The first term on the right becomes $\langle\Phi_{jk}^{bc}|\hat{P}_\alpha|\Phi_i^a\rangle$, but this element can only be non-zero, if the two wavefunctions differ by only one spin-orbital. This implies that a is either equal to b or c and i is equal to either j or k. The only contributions are then of the form

$$\pm\langle\Phi_{il}^{ad}|\hat{P}_\alpha|\Phi_i^a\rangle = \pm\langle\psi_d|\hat{P}|\psi_l\rangle$$

where the plus sign applies if ai matches one of the sets bj or ck, and the minus if it matches at mix of them (like $a = b$, $i = k$). dl is the remaining set of indexes. In the second term $\hat{q}_{ai}^{\dagger}$ can only perform the deexcitation in the bra if a is either b or c and i is either j or k. In this case we similarly only get contributions of the form

$$\pm\langle\Phi_l^d|\hat{P}|\Phi_0^{SCF}\rangle = \pm\langle\psi_d|\hat{P}|\psi_l\rangle$$

The two contributions will therefore cancel exactly, and the first order contribution to the property gradient vanishes.

10.5 We consider first contributions of the fluctuation operator $\hat{V}$ to the **A** matrix:

$$\langle\Phi^{\mathrm{MP}}|[q_{ai}, [\hat{V}, q_{bj}^{\dagger}]]|\Phi^{\mathrm{MP}}\rangle^{(2)}$$

Since $\hat{V}$ is of first order, we need to consider only terms, where one of the wavefunctions is the MP first order correction to wavefunction and the other is Φ^{SCF}. If we insert thus Φ^{MP1} e.g. in the ket and expand the commutators we get contributions, which involve the following matrix elements:

$$\begin{aligned}&\langle\Phi^{\mathrm{SCF}}|q_{ai}\hat{V}q_{bj}^{\dagger}|\Phi_{kl}^{cd}\rangle\\ -\,&\langle\Phi^{\mathrm{SCF}}|q_{ai}q_{bj}^{\dagger}\hat{V}|\Phi_{kl}^{cd}\rangle\\ -\,&\langle\Phi^{\mathrm{SCF}}|\hat{V}q_{bj}^{\dagger}q_{ai}|\Phi_{kl}^{cd}\rangle\\ &\underbrace{\langle\Phi^{\mathrm{SCF}}|q_{bj}^{\dagger}}_{=0}\hat{V}q_{ai}|\Phi_{kl}^{cd}\rangle\end{aligned}$$

The first term gives contributions of the kind $\langle\Phi_i^a|\hat{V}|\Phi_{jkl}^{bcd}\rangle$, while the second and third gives contributions of the kind $\langle\Phi^{\mathrm{SCF}}|\hat{V}|\Phi_{jk}^{bc}\rangle$. We should also consider the terms coming from using Φ^{MP1} as bra. In this case all contributions, where q_{ai} acts on the ket, vanish and we obtain only:

$$\begin{aligned} &\langle \Phi_{kl}^{cd} | q_{ai} \hat{V} q_{bj}^{\dagger} | \Phi^{\text{SCF}} \rangle \\ -&\langle \Phi_{kl}^{cd} | q_{ai} q_{bj}^{\dagger} \hat{V} | \Phi^{\text{SCF}} \rangle \end{aligned}$$

However, these are the same kind of contributions as before, if we remember that $\hat{V}$ is hermitian.

The corresponding contributions to the **B** matrix are of the type

$$\langle \Phi^{\text{MP}} | [q_{ai}, [\hat{V}, q_{bj}]] | \Phi^{\text{MP}} \rangle^{(2)}$$

Let's first consider the case, where the MP1 correction is in the bra and the ket is the SCF wavefunction. Three of the terms will then include operators trying to de-excite the SCF wavefunction, which is not possible. This leaves us with the term

$$-\langle \Phi_{kl}^{cd} | q_{ai} q_{bj} \hat{V} | \Phi^{\text{SCF}} \rangle$$

where however, the bra state becomes a quadruply excited determinant, which gives a vanishing matrix element due to the Slater-Condon rules. In the other case, having the MP1 correction as ket, we have:

$$\begin{aligned} &\langle \Phi^{\text{SCF}} | q_{ai} \hat{V} q_{bj} | \Phi_{kl}^{cd} \rangle \\ -&\langle \Phi^{\text{SCF}} | q_{ai} q_{bj} \hat{V} | \Phi_{kl}^{cd} \rangle \\ -&\langle \Phi^{\text{SCF}} | \hat{V} q_{bj} q_{ai} | \Phi_{kl}^{cd} \rangle \\ &\langle \Phi^{\text{SCF}} | q_{bj} \hat{V} q_{ai} | \Phi_{kl}^{cd} \rangle \end{aligned}$$

The first and last terms will give contributions of the type $\langle \Phi_i^a | \hat{V} | \Phi_l^d \rangle$, while the second term will give contributions of the type $\langle \Phi_{ij}^{ab} | \hat{V} | \Phi_{kl}^{cd} \rangle$. The third term finally will give a contribution as in the SCF energy $\langle \Phi^{\text{SCF}} | \hat{V} | \Phi^{\text{SCF}} \rangle$ but multiplied by first order double correlation coefficients.

Solutions to Chapter 11

11.1 We express the perturbed orbitals $\psi_i(\vec{r}, \vec{\mathcal{F}})$ as linear combinations of the unperturbed orbitals $\psi_q(\vec{r})$:

$$\psi_i(\vec{r}, \vec{\mathcal{F}}) = \sum_q^{\text{all}} \psi_q(\vec{r}) U_{qi}(\vec{\mathcal{F}})$$

and require that the perturbed orbitals remain orthogonal:

$$\langle \psi_i(\vec{r}, \vec{\mathcal{F}}) \mid \psi_j(\vec{r}, \vec{\mathcal{F}}) \rangle = \delta_{ij}$$

Combining the above equations we get

$$\begin{aligned}
\delta_{ij} &= \sum_{pq} U^*_{pi}(\vec{\mathcal{F}}) \underbrace{\langle \psi_p(\vec{r}) \mid \psi_q(\vec{r}) \rangle}_{\delta_{pq}} U_{qj}(\vec{\mathcal{F}}) \\
&= \sum_q U_{qi}(\vec{\mathcal{F}})^* U_{qj}(\vec{\mathcal{F}})
\end{aligned}$$

which is the orthogonality condition of the perturbed orbitals.

11.2 The perturbed Fock matrix is in the basis of the unperturbed orbitals given by

$$F_{pq}(\vec{\mathcal{F}}) = \langle \psi_p \,|\, \hat{f}(\vec{\mathcal{F}}) \,|\, \psi_q \rangle$$

where the perturbed Fock operator is given as

$$\hat{f}(\vec{\mathcal{F}}) = \hat{h}^{(0)} + \hat{h}^{(1)}(\vec{\mathcal{F}}) + \hat{h}^{(2)}(\vec{\mathcal{F}}) + \hat{v}^{HF}(\vec{\mathcal{F}})$$

Here the Hartree-Fock potential depends on the external field, because it depends on the occupied perturbed orbitals. The matrix element of the Hartree-Fock potential in the basis of the unperturbed orbitals is thus.

$$\begin{aligned}
\langle \psi_p \,|\, \hat{v}^{HF}(\vec{\mathcal{F}}) \,|\, \psi_q \rangle &= \sum_j^{\text{occ}} \Big\{ \langle \psi_p \psi_j(\vec{\mathcal{F}}) \mid \psi_q \psi_j(\vec{\mathcal{F}}) \rangle - \langle \psi_p \psi_j(\vec{\mathcal{F}}) \mid \psi_j(\vec{\mathcal{F}}) \psi_q \rangle \Big\} \\
&= \sum_j^{\text{occ}} \sum_{st}^{\text{all}} U^*_{sj}(\vec{\mathcal{F}}) \left\{ \langle \psi_p \psi_s \mid \psi_q \psi_t \rangle - \langle \psi_p \psi_s \mid \psi_t \psi_q \rangle \right\} U_{tj}(\vec{\mathcal{F}}) \\
&= \sum_j^{\text{occ}} \sum_{st}^{\text{all}} U^*_{sj}(\vec{\mathcal{F}}) \left\{ (\psi_p \psi_q \mid \psi_s \psi_t) - (\psi_p \psi_t \mid \psi_s \psi_q) \right\} U_{tj}(\vec{\mathcal{F}})
\end{aligned}$$

Inserting the above in the definition of the perturbed Fock matrix gives

$$F_{pq}(\vec{\mathcal{F}}) = \langle \psi_p \,|\, \hat{h}^{(0)} + \hat{h}^{(1)}(\vec{\mathcal{F}}) + \hat{h}^{(2)}(\vec{\mathcal{F}}) \,|\, \psi_q \rangle\rangle$$
$$+ \sum_j^{\text{occ}} \sum_{st}^{\text{all}} U^*_{sj}(\vec{\mathcal{F}}) \left\{ (\psi_p\psi_q|\psi_s\psi_t) - (\psi_p\psi_t|\psi_s\psi_q) \right\} U_{tj}(\vec{\mathcal{F}})$$

11.3 The Fock and coefficient matrices can be expanded in orders of the perturbation:

$$F_{pq}(\vec{\mathcal{F}}) = \underbrace{F^{(0)}_{pq}}_{\delta_{pq}\epsilon_p} + \sum_{\alpha\cdots} F^{(1)}_{\alpha\cdots,pq} \mathcal{F}_{\alpha\cdots} + \ldots$$
$$U_{qi}(\vec{\mathcal{F}}) = \underbrace{U^{(0)}_{qi}}_{\delta_{qi}} + \sum_{\alpha\cdots} U^{(1)}_{\alpha\cdots,qi} \mathcal{F}_{\alpha\cdots} + \ldots$$

An expression for $F^{(1)}_{\alpha\cdots,pq}$ is thus obtained by expanding the expression for $F_{pq}(\vec{\mathcal{F}})$ and collecting the terms of first order, *i.e.* linear in the applied field $\mathcal{F}_{\alpha\cdots}$. We use the expression obtained in the previous exercise, remembering that since we use the unperturbed functions as a basis, we only need to expand the operators and matrices.

$$\sum_{\alpha\cdots} F^{(1)}_{\alpha\cdots,pq} \mathcal{F}_{\alpha\cdots} = \langle \psi_p \,|\, \hat{h}^{(1)}(\vec{\mathcal{F}}) \,|\, \psi_q \rangle$$
$$+ \sum_j^{\text{occ}} \sum_{st}^{\text{all}} \left\{ (\psi_p\psi_q|\psi_s\psi_t) - (\psi_p\psi_t|\psi_s\psi_q) \right\} \left(U^*_{sj}(\vec{\mathcal{F}}) U_{tj}(\vec{\mathcal{F}}) \right)^{(1)}$$

The one electron part is easily obtained using that

$$\hat{h}^{(1)}(\vec{\mathcal{F}}) = \sum_{\alpha\cdots} \hat{o}^{\mathcal{F}}_{\alpha\cdots} \mathcal{F}_{\alpha\cdots}$$

meaning that we have in first order the integral $\langle \psi_p \mid \hat{o}^{\mathcal{F}}_{\alpha\cdots} \mid \psi_q \rangle$. For the two electron part, we see that

$$U^*_{sj}(\vec{\mathcal{F}}) U_{tj}(\vec{\mathcal{F}}) = \delta_{sj}\delta_{tj} + \sum_{\alpha\cdots} \left(U^{(1)*}_{\alpha\cdots,sj}\ \delta_{tj} + \delta_{sj}\ U^{(1)}_{\alpha\cdots,tj} \right) \mathcal{F}_{\alpha\cdots} + \cdots$$

Taking the first-order term and inserting in the expansion of the Fock matrix we get

$$F^{(1)}_{\alpha\cdots,pq} = \langle \psi_p \,|\, \hat{o}^{\mathcal{F}}_{\alpha\cdots} \,|\, \psi_q \rangle$$
$$+ \sum_j^{\text{occ}} \sum_{st}^{\text{all}} \left\{ (\psi_p\psi_q|\psi_s\psi_t) - (\psi_p\psi_t|\psi_s\psi_q) \right\} \left(U^{(1)*}_{\alpha\cdots,sj}(\vec{\mathcal{F}})\ \delta_{tj} + \delta_{sj}\ U^{(1)}_{\alpha\cdots,tj}(\vec{\mathcal{F}}) \right)$$

The summation over all orbitals in the first-order Fock matrix can be reduced to the summation over only all virtual orbitals. This can be shown by splitting the summation in the part over the occupied and over the virtual orbitals, *i.e.*

$$\sum_{j}^{\text{occ}}\sum_{st}^{\text{all}}\left\{U^{(1)*}_{\alpha\cdots,sj}(\vec{\mathcal{F}})\delta_{tj}+\delta_{sj}U^{(1)}_{\alpha\cdots,tj}(\vec{\mathcal{F}})\right\}\left(\psi_p\,\psi_q\middle|\middle|\psi_s\,\psi_t\right)$$
$$=\sum_{js}^{\text{occ}}U^{(1)*}_{\alpha\cdots,sj}(\vec{\mathcal{F}})\left(\psi_p\,\psi_q\middle|\middle|\psi_s\,\psi_j\right)+\sum_{jt}^{\text{occ}}\left(\psi_p\,\psi_q\middle|\middle|\psi_j\,\psi_t\right)U^{(1)}_{\alpha\cdots,tj}(\vec{\mathcal{F}})$$
$$+\sum_{j}^{\text{occ}}\sum_{st}^{\text{vir}}\left\{U^{(1)*}_{\alpha\cdots,sj}(\vec{\mathcal{F}})\delta_{tj}+\delta_{sj}U^{(1)}_{\alpha\cdots,tj}(\vec{\mathcal{F}})\right\}\left(\psi_p\,\psi_q\middle|\middle|\psi_s\,\psi_t\right)$$

where we have used the following short notation for the combination of a Coulomb and exchange two electron integral

$$\left(\psi_p\,\psi_q\middle|\middle|\psi_s\,\psi_t\right)=\left(\psi_p\,\psi_q\middle|\psi_s\,\psi_t\right)-\left(\psi_p\,\psi_t\middle|\psi_s\,\psi_q\right)$$

As the unperturbed orbitals can be chosen to be real, we can interchange j and s in the integral in the first sum. Furthermore we can rename the summation index from s to t and obtain for the two summations over occupied orbitals

$$\sum_{jt}^{\text{occ}}U^{(1)*}_{\alpha\cdots,tj}(\vec{\mathcal{F}})\left(\psi_p\,\psi_q\middle|\middle|\psi_j\,\psi_t\right)+\sum_{jt}^{\text{occ}}\left(\psi_p\,\psi_q\middle|\middle|\psi_j\,\psi_t\right)U^{(1)}_{\alpha\cdots,tj}(\vec{\mathcal{F}})$$

Finally according to Eq. (11.20) is $U^{(1)*}_{\alpha\cdots,tj}(\vec{\mathcal{F}})=-U^{(1)}_{\alpha\cdots,tj}(\vec{\mathcal{F}})$, which shows that the two summations of the occupied orbitals cancel each other and the first-order Fock matrix can be written as

$$F^{(1)}_{\alpha\cdots,pq}=\langle\psi_p\,|\,\hat{o}^{\mathcal{F}}_{\alpha\cdots}\,|\,\psi_q\rangle$$
$$+\sum_{j}^{\text{occ}}\sum_{st}^{\text{vir}}\left\{U^{(1)*}_{\alpha\cdots,sj}(\vec{\mathcal{F}})\delta_{tj}+\delta_{sj}U^{(1)}_{\alpha\cdots,tj}(\vec{\mathcal{F}})\right\}\{(\psi_p\psi_q|\psi_s\psi_t)-(\psi_p\psi_t|\psi_s\psi_q)\}$$

11.4 In order to obtain the Hartree-Fock energy to a certain order in the perturbation starting from Eq. (11.26), we need to obtain the orbital energy to the same order. We start therefore from the perturbed Hartree-Fock equations, Eq. (11.6):

$$\sum_{q}^{\text{all}}F_{rq}(\vec{\mathcal{F}})U_{qi}(\vec{\mathcal{F}})=\epsilon_i(\vec{\mathcal{F}})U_{ri}(\vec{\mathcal{F}})$$

We can expand the matrices in orders of the perturbation and collect the terms of second order. For simplicity we will use a shorter notation than in chapter 11.1, *i.e.* we will abbreviate $\sum_{\alpha\cdots}\epsilon^{(n)}_{\alpha\cdots,i}\,\mathcal{F}_{\alpha\cdots}$ by $\epsilon^{(n)}_i(\vec{\mathcal{F}})$ and similarly $\sum_{\alpha\cdots}U^{(n)}_{\alpha\cdots,qi}\,\mathcal{F}_{\alpha\cdots}$ by $U^{(n)}_{qi}(\vec{\mathcal{F}})$ or the Fock matrices by $F^{(n)}_{rq}(\vec{\mathcal{F}})$. The second-order equation reads then

$$\sum_q^{\text{all}} F_{rq}^{(2)}(\vec{\mathcal{F}})U_{qi}^{(0)}(\vec{\mathcal{F}}) + \sum_q^{\text{all}} F_{rq}^{(1)}(\vec{\mathcal{F}})U_{qi}^{(1)}(\vec{\mathcal{F}}) + \sum_q^{\text{all}} F_{rq}^{(0)}U_{qi}^{(2)}(\vec{\mathcal{F}})$$
$$= \epsilon_i^{(2)}(\vec{\mathcal{F}})U_{ri}^{(0)} + \epsilon_i^{(1)}(\vec{\mathcal{F}})U_{ri}^{(1)}(\vec{\mathcal{F}}) + \epsilon_i^{(0)}U_{ri}^{(2)}(\vec{\mathcal{F}})$$

Since the perturbed orbitals are expressed in the basis of the unperturbed ones, the zeroth-order orbital parameter matrix is a unit matrix, $U_{ri}^{(0)} = \delta_{ri}$. From this we see that $\epsilon_i^{(2)}(\vec{\mathcal{F}})U_{ri}^{(0)}$ vanishes in the equation above unless $r = i$. And since we are deriving an expression for $\epsilon_i^{(2)}(\vec{\mathcal{F}})$, we have to consider only the case $r = i$ in the equation above.

$$\epsilon_i^{(2)}(\vec{\mathcal{F}})$$
$$= F_{ii}^{(2)}(\vec{\mathcal{F}}) + \sum_q^{\text{all}} \left\{ F_{iq}^{(1)}(\vec{\mathcal{F}}) - \delta_{qi}\epsilon_i^{(1)}(\vec{\mathcal{F}}) \right\} U_{qi}^{(1)}(\vec{\mathcal{F}}) + \sum_q^{\text{all}} \left\{ F_{iq}^{(0)} - \delta_{qi}\epsilon_i^{(0)} \right\} U_{qi}^{(2)}(\vec{\mathcal{F}})$$

But as the zeroth-order Fock matrix is diagonal in the basis of the unperturbed orbitals and the diagonal elements are the unperturbed orbital energies the last term on the right hand side vanishes leading to

$$\epsilon_i^{(2)}(\vec{\mathcal{F}}) = F_{ii}^{(2)}(\vec{\mathcal{F}}) + \sum_q^{\text{all}} \left\{ F_{iq}^{(1)}(\vec{\mathcal{F}}) - \delta_{qi}\epsilon_i^{(1)}(\vec{\mathcal{F}}) \right\} U_{qi}^{(1)}(\vec{\mathcal{F}})$$

If we introduce the following short notation for the combination of a Coulomb and exchange two electron integral

$$\big(\psi_p\,\psi_q\big|\big|\psi_s\,\psi_t\big) = \big(\psi_p\,\psi_q\big|\psi_s\,\psi_t\big) - \big(\psi_p\,\psi_t\big|\psi_s\,\psi_q\big)$$

and make use of the solution to exercise (11.2), we can write the required elements of the perturbed Fock matrices as

$$F_{ii}^{(2)}(\vec{\mathcal{F}}) = \langle\psi_i\,|\,\hat{h}^{(2)}\,|\,\psi_i\rangle$$
$$+ \sum_j^{\text{occ}} \sum_{st}^{\text{all}} \left\{ U_{sj}^{(2)*}(\vec{\mathcal{F}})\delta_{tj} + \delta_{sj}U_{tj}^{(2)}(\vec{\mathcal{F}}) + U_{sj}^{(1)*}(\vec{\mathcal{F}})U_{tj}^{(1)}(\vec{\mathcal{F}}) \right\} \big(\psi_i\,\psi_i\big|\big|\psi_s\,\psi_t\big)$$

$$F_{iq}^{(1)}(\vec{\mathcal{F}}) = \langle\psi_i\,|\,\hat{h}^{(1)}\,|\,\psi_q\rangle + \sum_j^{\text{occ}} \sum_{st}^{\text{all}} \left\{ U_{sj}^{(1)*}(\vec{\mathcal{F}})\delta_{tj} + \delta_{sj}U_{tj}^{(1)}(\vec{\mathcal{F}}) \right\} \big(\psi_i\,\psi_q\big|\big|\psi_s\,\psi_t\big)$$

The second-order orbital energy becomes then

$$
\begin{aligned}
&\epsilon_i^{(2)}(\vec{\mathcal{F}}) \\
&= \langle\psi_i\,|\,\hat{h}^{(2)}\,|\,\psi_i\rangle + \sum_j^{\text{occ}}\sum_{st}^{\text{all}}\left\{U_{sj}^{(2)*}(\vec{\mathcal{F}})\delta_{tj} + \delta_{sj}U_{tj}^{(2)}(\vec{\mathcal{F}}) + U_{sj}^{(1)*}(\vec{\mathcal{F}})U_{tj}^{(1)}(\vec{\mathcal{F}})\right\}\left(\psi_i\,\psi_i\big|\big|\psi_s\,\psi_t\right) \\
&\quad + \sum_q^{\text{all}}\left[\left\{\langle\psi_i\,|\,\hat{h}^{(1)}\,|\,\psi_q\rangle + \sum_j^{\text{occ}}\sum_{st}^{\text{all}}\left\{U_{sj}^{(1)*}(\vec{\mathcal{F}})\delta_{tj} + \delta_{sj}U_{tj}^{(1)}(\vec{\mathcal{F}})\right\}\left(\psi_i\,\psi_q\big|\big|\psi_s\,\psi_t\right)\right\}\right. \\
&\qquad\qquad \left. - \delta_{qi}\epsilon_i^{(1)}(\vec{\mathcal{F}})\right]U_{qi}^{(1)}(\vec{\mathcal{F}})
\end{aligned}
$$

Now we are ready to combine this with the expression for the second-order energy, Eq. (11.26),

$$
E_0^{(2)}(\vec{\mathcal{F}}) = \sum_i^{\text{occ}}\epsilon_i^{(2)}(\vec{\mathcal{F}}) - \frac{1}{2}\sum_{ij}^{\text{occ}}\sum_{abcd}^{\text{all}}\left(\psi_a\psi_b\big|\big|\psi_c\psi_d\right)\left\{U_{ai}^*(\vec{\mathcal{F}})U_{cj}^*(\vec{\mathcal{F}})U_{bi}(\vec{\mathcal{F}})U_{dj}(\vec{\mathcal{F}})\right\}^{(2)}
$$

The contribution from the sum over the second-order orbital energies becomes

$$
\begin{aligned}
&\sum_i^{\text{occ}}\epsilon_i^{(2)}(\vec{\mathcal{F}}) = \sum_i^{\text{occ}}\langle\psi_i\,|\,\hat{h}^{(2)}\,|\,\psi_i\rangle \\
&+ \sum_{ij}^{\text{occ}}\sum_{st}^{\text{all}}\left\{U_{sj}^{(2)*}(\vec{\mathcal{F}})\delta_{tj} + \delta_{sj}U_{tj}^{(2)}(\vec{\mathcal{F}}) + U_{sj}^{(1)*}(\vec{\mathcal{F}})U_{tj}^{(1)}(\vec{\mathcal{F}})\right\}\left(\psi_i\,\psi_i\big|\big|\psi_s\,\psi_t\right) \\
&+ \sum_i^{\text{occ}}\sum_q^{\text{all}}\left[\left\{\langle\psi_i\,|\,\hat{h}^{(1)}\,|\,\psi_q\rangle + \sum_j^{\text{occ}}\sum_{st}^{\text{all}}\left\{U_{sj}^{(1)*}(\vec{\mathcal{F}})\delta_{tj} + \delta_{sj}U_{tj}^{(1)}(\vec{\mathcal{F}})\right\}\left(\psi_i\,\psi_q\big|\big|\psi_s\,\psi_t\right)\right\}\right. \\
&\qquad\qquad \left. - \delta_{qi}\epsilon_i^{(1)}(\vec{\mathcal{F}})\right]U_{qi}^{(1)}(\vec{\mathcal{F}})
\end{aligned}
$$

In addition, the second order correction to the SCF energy in Eq. (11.26) contains also the following term

$$
-\frac{1}{2}\sum_{ij}^{\text{occ}}\sum_{abcd}^{\text{all}}\left(\psi_a\,\psi_b\big|\big|\psi_c\,\psi_d\right)\left\{U_{ai}^*(\vec{\mathcal{F}})U_{cj}^*(\vec{\mathcal{F}})U_{bi}(\vec{\mathcal{F}})U_{dj}(\vec{\mathcal{F}})\right\}^{(2)}
$$

However, since the second-order corrections to the SCF energy in Eq. (11.27) contains no contribution from two-electron integrals, the above must cancel the terms with two-electron integrals in the expression for the second-order orbital energy. We will proof this in the following.

The part of the two-electron term in Eq. (11.27), that contains the second-order correction to the orbitals is:

$$-\frac{1}{2}\sum_{ij}^{\text{occ}}\sum_{abcd}^{\text{all}}\Big\{U_{ai}^{(2)*}(\vec{\mathcal{F}})\delta_{bi}\delta_{cj}\delta_{dj}+U_{cj}^{(2)*}(\vec{\mathcal{F}})\delta_{ai}\delta_{bi}\delta_{dj}$$
$$+U_{bi}^{(2)}(\vec{\mathcal{F}})\delta_{ai}\delta_{cj}\delta_{dj}+U_{dj}^{(2)}(\vec{\mathcal{F}})\delta_{ai}\delta_{bi}\delta_{cj}\Big\}\big(\psi_a\,\psi_b\big|\big|\psi_c\,\psi_d\big)$$

As we are summing over all i and j or a, b, c and d we can freely interchange them and write the following instead of

$$-\frac{1}{2}\sum_{ij}^{\text{occ}}\sum_{ab}^{\text{all}}2\Big\{U_{aj}^{(2)*}(\vec{\mathcal{F}})\delta_{bj}+\delta_{aj}U_{bj}^{(2)}(\vec{\mathcal{F}})\Big\}\big(\psi_i\,\psi_i\big|\big|\psi_a\,\psi_b\big)$$

which cancel the terms with second-order orbital coefficients in $\sum_i^{\text{occ}}\epsilon_i^{(2)}(\vec{\mathcal{F}})$.

Next we consider terms which contain the product of two first-order orbital coefficients, where neither of them are complex conjugated. From the second-order orbital energy we have:

$$\sum_{ij}^{\text{occ}}\sum_{stq}^{\text{all}}\delta_{sj}U_{tj}^{(1)}(\vec{\mathcal{F}})U_{qi}^{(1)}(\vec{\mathcal{F}})\big(\psi_i\,\psi_q\big|\big|\psi_s\,\psi_t\big)=\sum_{ij}^{\text{occ}}\sum_{tq}^{\text{all}}U_{tj}^{(1)}(\vec{\mathcal{F}})U_{qi}^{(1)}(\vec{\mathcal{F}})\big(\psi_i\,\psi_q\big|\big|\psi_j\,\psi_t\big)$$

From two-electron part of the Hartree-Fock energy we get

$$-\frac{1}{2}\sum_{ij}^{\text{occ}}\sum_{abcd}^{\text{all}}\Big\{\delta_{ai}U_{bi}^{(1)}(\vec{\mathcal{F}})\delta_{cj}U_{dj}^{(1)}(\vec{\mathcal{F}})+U_{ai}^{(1)*}(\vec{\mathcal{F}})\delta_{bi}U_{cj}^{(1)*}(\vec{\mathcal{F}})\delta_{dj}\Big\}\big(\psi_a\,\psi_b\big|\big|\psi_c\,\psi_d\big)$$

But according to Eq. (11.20) is $U_{ai}^{(1)*}(\vec{\mathcal{F}})=-U_{ai}^{(1)}(\vec{\mathcal{F}})$ and we obtain

$$-\frac{1}{2}\sum_{ij}^{\text{occ}}\sum_{abcd}^{\text{all}}\Big\{\delta_{ai}U_{bi}^{(1)}(\vec{\mathcal{F}})\delta_{cj}U_{dj}^{(1)}(\vec{\mathcal{F}})+U_{ai}^{(1)}(\vec{\mathcal{F}})\delta_{bi}U_{cj}^{(1)}(\vec{\mathcal{F}})\delta_{dj}\Big\}\big(\psi_a\,\psi_b\big|\big|\psi_c\,\psi_d\big)$$

and interchanging the indices and using that the unperturbed orbitals can be chosen to be real we obtain

$$-\frac{1}{2}\sum_{ij}^{\text{occ}}\sum_{ab}^{\text{all}}2U_{ai}^{(1)}(\vec{\mathcal{F}})U_{bj}^{(1)}(\vec{\mathcal{F}})\big(\psi_i\,\psi_a\big|\big|\psi_j\,\psi_b\big)$$

which cancels the corresponding term from the second-order orbital energy.

The remaining parts of the second-order energy are then

$$
\begin{aligned}
E_0^{(2)}(\vec{\mathcal{F}}) = {} & \sum_i^{\text{occ}} \langle \psi_i \,|\, \hat{h}^{(2)} \,|\, \psi_i \rangle + \sum_i^{\text{occ}} \sum_q^{\text{all}} \langle \psi_i \,|\, \hat{h}^{(1)} \,|\, \psi_q \rangle U_{qi}^{(1)}(\vec{\mathcal{F}}) \\
& + \sum_{ij}^{\text{occ}} \sum_{st}^{\text{all}} U_{sj}^{(1)*}(\vec{\mathcal{F}}) U_{tj}^{(1)}(\vec{\mathcal{F}}) \big(\psi_i \, \psi_i \big|\big| \psi_s \, \psi_t \big) \\
& + \sum_{ij}^{\text{occ}} \sum_{qst}^{\text{all}} U_{sj}^{(1)*}(\vec{\mathcal{F}}) \delta_{tj} U_{qi}^{(1)}(\vec{\mathcal{F}}) \big(\psi_i \, \psi_q \big|\big| \psi_s \, \psi_t \big) - \sum_i^{\text{occ}} \sum_q^{\text{all}} \delta_{qi} \epsilon_i^{(1)}(\vec{\mathcal{F}}) U_{qi}^{(1)}(\vec{\mathcal{F}}) \\
& - \frac{1}{2} \sum_{ij}^{\text{occ}} \sum_{abcd}^{\text{all}} \Big\{ U_{ai}^{(1)*} U_{bi}^{(1)} \delta_{cj} \delta_{dj} + U_{cj}^{(1)*} U_{dj}^{(1)} \delta_{ai} \delta_{bi} \\
& \qquad\qquad + U_{ai}^{(1)*} U_{dj}^{(1)} \delta_{cj} \delta_{bi} + U_{cj}^{(1)*} U_{bi}^{(1)} \delta_{ai} \delta_{dj} \Big\} (ab||cd)
\end{aligned}
$$

Interchanging again the summation indices in the summation over *abcd* in the last term, the four contributions in the last term can be shown to reduce to two contributions, which cancel the third and fourth term in the expression above, leaving us with

$$
E_0^{(2)}(\vec{\mathcal{F}}) = \sum_i^{\text{occ}} \langle \psi_i \,|\, \hat{h}^{(2)} \,|\, \psi_i \rangle + \sum_i^{\text{occ}} \sum_q^{\text{all}} \langle \psi_i \,|\, \hat{h}^{(1)} \,|\, \psi_q \rangle U_{qi}^{(1)}(\vec{\mathcal{F}}) - \sum_i^{\text{occ}} \epsilon_i^{(1)}(\vec{\mathcal{F}}) U_{ii}^{(1)}(\vec{\mathcal{F}})
$$

The total energy must be real, but the second and third terms might not be, so we replace them by their real parts

$$
\begin{aligned}
E_0^{(2)}(\vec{\mathcal{F}}) = {} & \sum_i^{\text{occ}} \langle \psi_i \,|\, \hat{h}^{(2)} \,|\, \psi_i \rangle + \frac{1}{2} \sum_i^{\text{occ}} \sum_q^{\text{all}} \Big\{ \langle \psi_i \,|\, \hat{h}^{(1)} \,|\, \psi_q \rangle U_{qi}^{(1)}(\vec{\mathcal{F}}) + \langle \psi_i \,|\, \hat{h}^{(1)} \,|\, \psi_q \rangle^* U_{qi}^{(1)*}(\vec{\mathcal{F}}) \Big\} \\
& - \frac{1}{2} \sum_i^{\text{occ}} \Big\{ \epsilon_i^{(1)}(\vec{\mathcal{F}}) U_{ii}^{(1)}(\vec{\mathcal{F}}) + \epsilon_i^{(1)*}(\vec{\mathcal{F}}) U_{ii}^{(1)*}(\vec{\mathcal{F}}) \Big\}
\end{aligned}
$$

The orbital energies are of course real, $\epsilon_i^{(1)*} = \epsilon_i^{(1)}$ and $U_{ii}^{(1)*}(\vec{\mathcal{F}}) = -U_{ii}^{(1)*}(\vec{\mathcal{F}})$ according to Eq. (11.20), which makes the term with the first-order orbital energies vanish. Using that $\hat{h}^{(1)}$ is an hermitian operator we have

$$
E_0^{(2)}(\vec{\mathcal{F}}) = \sum_i^{\text{occ}} \langle \psi_i \,|\, \hat{h}^{(2)} \,|\, \psi_i \rangle + \frac{1}{2} \sum_i^{\text{occ}} \sum_q^{\text{all}} \Big\{ \langle \psi_i \,|\, \hat{h}^{(1)} \,|\, \psi_q \rangle U_{qi}^{(1)}(\vec{\mathcal{F}}) + \langle \psi_q \,|\, \hat{h}^{(1)} \,|\, \psi_i \rangle U_{qi}^{(1)*}(\vec{\mathcal{F}}) \Big\}
$$

Finally, as in the solution to exercise (11.2), the summation or all q can be reduced to over all virtual orbitals

$$E_0^{(2)}(\vec{\mathcal{F}}) = \sum_i^{\text{occ}} \langle \psi_i \,|\, \hat{h}^{(2)} \,|\, \psi_i \rangle + \frac{1}{2} \sum_i^{\text{occ}} \sum_q^{\text{vir}} \left\{ \langle \psi_i \,|\, \hat{h}^{(1)} \,|\, \psi_q \rangle U_{qi}^{(1)}(\vec{\mathcal{F}}) + \langle \psi_q \,|\, \hat{h}^{(1)} \,|\, \psi_i \rangle U_{qi}^{(1)*}(\vec{\mathcal{F}}) \right\}$$

11.5 We can express the time-dependant MCSCF wavefunction as:

$$|\Phi_0^{MCSCF}(t)\rangle = e^{\imath\hat{\kappa}(t)} e^{\imath\hat{S}(t)} |\Phi_0^{MCSCF}\rangle$$

Inserting this in the Ehrenfest theorem applied to an MCSCF wavefunction, Eq. (11.40), we obtain

$$\begin{aligned} &\frac{d}{dt} \langle \Phi_0^{MCSCF} | e^{-\imath\hat{\kappa}(t)} e^{-\imath\hat{S}(t)} \hat{h}_j e^{\imath\hat{\kappa}(t)} e^{\imath\hat{S}(t)} | \Phi_0^{MCSCF} \rangle \\ &\quad + \frac{\imath}{\hbar} \langle \Phi_0^{MCSCF} | e^{-\imath\hat{\kappa}(t)} e^{-\imath\hat{S}(t)} [\hat{h}_j, \hat{H}^{(0)} + \hat{H}^{(1)}(t)] e^{\imath\hat{\kappa}(t)} e^{\imath\hat{S}(t)} | \Phi_0^{MCSCF} \rangle = 0 \end{aligned}$$

We need to expand the orbital rotation and state transfer operators in orders of the perturbation.

$$\begin{aligned} \hat{\kappa}(t) &= \hat{\kappa}^{(0)} + \hat{\kappa}^{(1)}(t) + \cdots \\ \hat{S}(t) &= \hat{S}^{(0)} + \hat{S}^{(1)}(t) + \cdots \end{aligned}$$

Where the time independent terms vanish, since the MCSCF wavefunction are optimized for the time-independent potential. The exponentials are not very convenient to work with, so we can expand the time-dependant part, retaining only terms to first order.

$$\left(e^{\imath\hat{\kappa}(t)} e^{\imath\hat{S}(t)} \right)^{(0,1)} = 1 + \imath\hat{\kappa}^{(1)}(t) + \imath\hat{S}^{(1)}(t)$$

Where the zero-order terms are independent of the perturbation and thus cannot change the wavefunction. The equation from the Ehrenfest theorem to atleast first order becomes:

$$\begin{aligned} &\frac{d}{dt} \langle \Phi_0^{MCSCF} | \left\{ 1 - \imath\hat{\kappa}^{(1)}(t) - \imath\hat{S}^{(1)}(t) \right\} \hat{h}_j \left\{ 1 + \imath\hat{\kappa}^{(1)}(t) + \imath\hat{S}^{(1)}(t) \right\} | \Phi_0^{MCSCF} \rangle \\ &+ \frac{\imath}{\hbar} \langle \Phi_0^{MCSCF} | \left\{ 1 - \imath\hat{\kappa}^{(1)}(t) - \imath\hat{S}^{(1)}(t) \right\} [\hat{h}_j, \hat{H}^{(0)} + \hat{H}^{(1)}(t)] \left\{ 1 + \imath\hat{\kappa}^{(1)}(t) + \imath\hat{S}^{(1)}(t) \right\} | \Phi_0^{MCSCF} \rangle \\ &= 0 \end{aligned}$$

Collection the first order terms and using the fact that Φ_0^{MCSCF} is time-independent we get the first order equation:

$$\begin{aligned} &\imath\hbar \langle \Phi_0^{MCSCF} | [\hat{h}_j, \frac{d}{dt}\hat{\kappa}^{(1)}(t) + \frac{d}{dt}\hat{S}^{(1)}(t)] | \Phi_0^{MCSCF} \rangle \\ &- \langle \Phi_0^{MCSCF} | [[\hat{h}_j, \hat{H}^{(0)}], \hat{\kappa}^{(1)}(t) + \hat{S}^{(1)}(t)] | \Phi_0^{MCSCF} \rangle \\ &\qquad = -\imath \langle \Phi_0^{MCSCF} | [\hat{h}_j, \hat{H}^{(1)}(t)] | \Phi_0^{MCSCF} \rangle \end{aligned}$$

11.6 The first order MCRPA equation can be written as

$$\imath\hbar \boldsymbol{S}\frac{d}{dt}\boldsymbol{\gamma}^{(1)}(t) - \boldsymbol{E}\boldsymbol{\gamma}^{(1)}(t) = \imath\, \boldsymbol{T}(\hat{H}^{(1)}(t))$$

and we can express the coefficient vector $\boldsymbol{\gamma}(t)$ in terms of it's Fourier components:

$$\boldsymbol{\gamma}^{(1)}(t) = \int_{-\infty}^{\infty} d\omega\, \boldsymbol{\gamma}^{(1)}(\omega) = -\frac{\imath}{2}\sum_{\beta\dots}\int_{-\infty}^{\infty} d\omega\, \mathbf{X}(\hat{O}^{\omega}_{\beta\dots})\mathcal{F}_{\beta\dots}(\omega)e^{-\imath\omega t}$$

And thus

$$\begin{aligned}\frac{d}{dt}\boldsymbol{\gamma}^{(1)}(t) &= \frac{d}{dt}\int_{-\infty}^{\infty} d\omega\, \boldsymbol{\gamma}^{(1)}(\omega) = \int_{-\infty}^{\infty}\frac{d}{dt} d\omega\, \boldsymbol{\gamma}^{(1)}(\omega)\\ &= -\frac{1}{2}\sum_{\beta\dots}\int_{-\infty}^{\infty} d\omega\, \mathbf{X}(\hat{O}^{\omega}_{\beta\dots})\mathcal{F}_{\beta\dots}(\omega)\omega e^{-\imath\omega t}\end{aligned}$$

since ω and t are different variables. We also need to decompose $\boldsymbol{T}(\hat{H}^{(1)}(t))$ into Fourier components:

$$\boldsymbol{T}(\hat{H}^{(1)}(t)) = -\frac{\imath}{2}\sum_{\beta\dots}\int_{-\infty}^{\infty} d\omega\, \boldsymbol{T}(\hat{O}^{\omega}_{\beta\dots})\mathcal{F}_{\beta\dots}(\omega)e^{-\imath\omega t}$$

And we obtain

$$\begin{aligned}&-\frac{\imath}{2}\sum_{\beta\dots}\int_{-\infty}^{\infty} d\omega\, \left(\hbar\omega\boldsymbol{S} - \boldsymbol{E}\right)\mathbf{X}(\hat{O}^{\omega}_{\beta\dots})\mathcal{F}_{\beta\dots}(\omega)e^{-\imath\omega t}\\ &\qquad = -\frac{\imath}{2}\sum_{\beta\dots}\int_{-\infty}^{\infty} d\omega\, \boldsymbol{T}(\hat{O}^{\omega}_{\beta\dots})\mathcal{F}_{\beta\dots}(\omega)e^{-\imath\omega t}\end{aligned}$$

We require that the above equation must be true for any value of the frequency ω. We can therefore remove the integration over ω and equate the terms linear in the component $\mathcal{F}_{\beta\dots}$ of the external field, *i.e.*

$$(\hbar\omega\boldsymbol{S} - \boldsymbol{E})\mathbf{X}(\hat{O}^{\omega}_{\beta\dots}) = \boldsymbol{T}(\hat{O}^{\omega}_{\beta\dots})$$

11.7 We can express the time-dependant Møller-Plesset wavefunction as:

$$|\Phi_0^{MP}(t)\rangle = e^{\imath\hat{\kappa}(t)}e^{\imath\hat{S}(t)}|\Phi_0^{MP}\rangle$$

Inserting this in the Ehrenfest theorem applied to an Møller-Plesset wavefunction, Eq. (11.55), we obtain

$$\begin{aligned}&\frac{d}{dt}\langle\Phi_0^{MP}|e^{-\imath\hat{\kappa}(t)}e^{-\imath\hat{S}(t)}\hat{h}_j e^{\imath\hat{\kappa}(t)}e^{\imath\hat{S}(t)}|\Phi_0^{MP}\rangle\\ &\quad +\frac{\imath}{\hbar}\langle\Phi_0^{MP}|e^{-\imath\hat{\kappa}(t)}e^{-\imath\hat{S}(t)}[\hat{h}_j, \hat{H}^{(0)} + \hat{H}^{(1)}(t)]e^{\imath\hat{\kappa}(t)}e^{\imath\hat{S}(t)}|\Phi_0^{MP}\rangle = 0\end{aligned}$$

Expanding the exponentials like in exercise 11.5 to first order, the first-order Ehrenfest equation becomes

$$\begin{aligned}
&\imath\hbar\langle\Phi_0^{MP}|[\hat{h}_j, \frac{d}{dt}\hat{\kappa}^{(1)}(t) + \frac{d}{dt}\hat{S}^{(1)}(t)]|\Phi_0^{MP}\rangle \\
&\qquad - \langle\Phi_0^{MP}|[[\hat{h}_j, \hat{H}^{(0)}], \hat{\kappa}^{(1)}(t) + \hat{S}^{(1)}(t)]|\Phi_0^{MP}\rangle \\
&\qquad = -\imath\langle\Phi_0^{MP}|[\hat{h}_j, \hat{H}^{(1)}(t)]|\Phi_0^{MP}\rangle
\end{aligned}$$

Combining the orbital rotation and high-order excitation operators in one row vector $\hat{h}^T$ and the coefficients in one column-vector $\boldsymbol{\gamma}(t)$ again

$$\hat{\kappa}(t) + \hat{S}(t) = \hat{\boldsymbol{h}}^T\boldsymbol{\gamma}(t)$$

the first-order Ehrenfest equation can be written as

$$\begin{aligned}
\imath\hbar\langle\Phi_0^{MP}|[\hat{h}_j, \hat{\boldsymbol{h}}^T\frac{d}{dt}\boldsymbol{\gamma}^{(1)}(t)]|\Phi_0^{MP}\rangle - \langle\Phi_0^{MP}|[[\hat{h}_j, \hat{H}^{(0)}], \hat{\boldsymbol{h}}^T\boldsymbol{\gamma}^{(1)}(t)]|\Phi_0^{MP}\rangle \\
= -\imath\langle\Phi_0^{MP}|[\hat{h}_j, \hat{H}^{(1)}(t)]|\Phi_0^{MP}\rangle
\end{aligned}$$

or collecting the first-order Ehrenfest equations for all operators $\hat{h}_j$ as rows of an matrix equation

$$\begin{aligned}
\imath\hbar\langle\Phi_0^{MP}|[\hat{\boldsymbol{h}}^\dagger, \hat{\boldsymbol{h}}^T]|\Phi_0^{MP}\rangle\frac{d}{dt}\boldsymbol{\gamma}^{(1)}(t) - \langle\Phi_0^{MP}|[[\hat{\boldsymbol{h}}^\dagger, \hat{H}^{(0)}], \hat{\boldsymbol{h}}^T]|\Phi_0^{MP}\rangle\boldsymbol{\gamma}^{(1)}(t) \\
= -\imath\langle\Phi_0^{MP}|[\hat{\boldsymbol{h}}^\dagger, \hat{H}^{(1)}(t)]|\Phi_0^{MP}\rangle
\end{aligned}$$

Identifying the electronic Hessian matrices $\boldsymbol{E}$ and the overlap $\boldsymbol{S}$, Eq. (3.162) and Eq. (3.163), as well as the property gradient vector $\boldsymbol{T}(\hat{H}^{(1)}(t))$, Eq. (3.160), we can write the first-order Ehrenfest equation more compact

$$\imath\hbar\boldsymbol{S}\frac{d}{dt}\boldsymbol{\gamma}^{(1)}(t) - \boldsymbol{E}\boldsymbol{\gamma}^{(1)}(t) = -\imath\,\boldsymbol{T}(\hat{H}^{(1)}(t))$$

The rest of the derivation goes exactly like in exercise 11.6.

11.8 The time dependant coupled cluster and lambda states are given as

$$\begin{aligned}
|\Phi_0^{CC}(t)\rangle &= e^{\hat{T}(t)}e^{\imath\frac{\epsilon(t)}{\hbar}}|\Phi_0^{SCF}\rangle \\
\langle\Phi_0^{\Lambda}(t)| &= \langle\Phi_0^{SCF}|\left[1 + \hat{\Lambda}(t)\right]e^{-\hat{T}(t)}e^{-\imath\frac{\epsilon(t)}{\hbar}}
\end{aligned}$$

We start by looking at the the right hand coupled cluster Schrödinger equation

$$e^{-\hat{T}(t)}\imath\hbar\frac{d}{dt}|\Phi_0^{CC}(t)\rangle = e^{-\hat{T}(t)}\hat{H}(t)|\Phi_0^{CC}(t)\rangle$$

Evaluating the time derivative on the left hand side, we see that

$$\begin{aligned}
\frac{d}{dt}|\Phi_0^{CC}(t)\rangle &= \frac{d}{dt}e^{\hat{T}(t)}|\Phi_0^{SCF}\rangle e^{\imath\frac{\epsilon(t)}{\hbar}} \\
&= e^{\hat{T}(t)}\sum_{j_\nu}\frac{\partial\hat{T}}{\partial t_{j_\nu}}\frac{dt_{j_\nu}(t)}{dt}|\Phi_0^{SCF}\rangle e^{\imath\frac{\epsilon(t)}{\hbar}} + e^{\hat{T}(t)}e^{\imath\frac{\epsilon(t)}{\hbar}}|\Phi_0^{SCF}\rangle\frac{\imath}{\hbar}\frac{d\epsilon(t)}{dt}
\end{aligned}$$

Remembering that $\frac{\partial \hat{T}}{\partial t_{j_\nu}} = {}^e\hat{h}_{j_\nu}$ and projecting from the left with the state $\langle\Phi_0^{SCF}|{}^d\hat{h}_{i_\mu}$ we get:

$$\imath\hbar\sum_{j_\nu}\langle\Phi_0^{SCF}|{}^d\hat{h}_{i_\mu}e^{-\hat{T}(t)}e^{\hat{T}(t)e}\hat{h}_{j_\nu}|\Phi_0^{SCF}\rangle\frac{dt_{j_\nu}(t)}{dt}e^{\imath\frac{\epsilon(t)}{\hbar}} - \langle\Phi_0^{SCF}|{}^d\hat{h}_{i_\mu}|\Phi_0^{SCF}\rangle\frac{d\epsilon(t)}{dt}e^{\imath\frac{\epsilon(t)}{\hbar}}$$

$$= \langle\Phi_0^{SCF}|{}^d\hat{h}_{i_\mu}e^{-\hat{T}(t)}\hat{H}(t)|\Phi_0^{CC}(t)\rangle$$

The first matrix element on the left hand side can be evaluated as:

$$\langle\Phi_0^{SCF}|{}^d\hat{h}_{i_\mu}e^{-\hat{T}(t)}e^{\hat{T}(t)e}\hat{h}_{j_\nu}|\Phi_0^{SCF}\rangle = \langle\Phi_0^{SCF}|{}^d\hat{h}_{i_\mu}{}^e\hat{h}_{j_\nu}|\Phi_0^{SCF}\rangle = \delta_{i_\mu j_\nu}$$

while the second matrix element is the overlap between the SCF ground state and a singly excited determinant is thus zero. Removing the phase factors on both sides we obtain the desired equation for the amplitudes:

$$\imath\hbar\frac{dt_{i_\mu}(t)}{dt} = \langle\Phi_0^{SCF}|{}^d\hat{h}_{i_\mu}e^{-\hat{T}(t)}\hat{H}(t)e^{\hat{T}(t)}|\Phi_0^{SCF}\rangle$$

If we instead project against the SCF ground state on the left, all the terms that include the derivative of the amplitudes will vanish, and we obtain the following equation for the time derivative of the phase factor:

$$\frac{d\epsilon(t)}{dt} = -\langle\Phi_0^{SCF}|e^{-\hat{T}(t)}\hat{H}(t)e^{\hat{T}(t)}|\Phi_0^{SCF}\rangle$$

We now turn our attention to the left hand coupled cluster Schrödinger equation

$$-\imath\hbar\left(\frac{d}{dt}\langle\Phi_0^{SCF}|\left[1+\hat{\Lambda}(t)\right]e^{-\hat{T}(t)}e^{-\imath\frac{\epsilon(t)}{\hbar}}\right)e^{\hat{T}(t)} = \langle\Phi_0^{\Lambda}(t)|\hat{H}(t)e^{\hat{T}(t)}$$

Evaluating the derivative we get:

$$\frac{d}{dt}\langle\Phi_0^{SCF}|\left[1+\hat{\Lambda}(t)\right]e^{-\hat{T}(t)}e^{-\imath\frac{\epsilon(t)}{\hbar}} = \sum_{j_\nu}\langle\Phi_0^{SCF}|\frac{\partial\hat{\Lambda}}{\partial\lambda_{j_\nu}}\frac{d\lambda_{j_\nu}(t)}{dt}e^{-\hat{T}(t)}e^{-\imath\frac{\epsilon(t)}{\hbar}}$$

$$-\sum_{j_\nu}\langle\Phi_0^{SCF}|\left[1+\hat{\Lambda}(t)\right]e^{-\hat{T}(t)}\frac{\partial\hat{T}}{\partial t_{j_\nu}}\frac{dt_{j_\nu}(t)}{dt}e^{-\imath\frac{\epsilon(t)}{\hbar}}$$

$$-\frac{\imath}{\hbar}\langle\Phi_0^{SCF}|\left[1+\hat{\Lambda}(t)\right]e^{-\hat{T}}e^{-\imath\frac{\epsilon(t)}{\hbar}}\frac{d\epsilon(t)}{dt}$$

Inserting $\frac{\partial\hat{\Lambda}}{\partial\lambda_{j_\nu}} = {}^d\hat{h}_{j_\nu}$ and $\frac{\partial \hat{T}}{\partial t_{j_\nu}} = {}^e\hat{h}_{j_\nu}$ the left hand coupled cluster Schrödinger equation becomes

$$-\imath\hbar\sum_{j_\nu}\langle\Phi_0^{SCF}|{}^d\hat{h}_{j_\nu}\frac{d\lambda_{j_\nu}(t)}{dt}e^{-\imath\frac{\epsilon(t)}{\hbar}} + \imath\hbar\sum_{j_\nu}\langle\Phi_0^{SCF}|\left[1+\hat{\Lambda}(t)\right]{}^e\hat{h}_{j_\nu}\frac{dt_{j_\nu}(t)}{dt}e^{-\imath\frac{\epsilon(t)}{\hbar}}$$

$$-\langle\Phi_0^{SCF}|\left[1+\hat{\Lambda}(t)\right]e^{-\imath\frac{\epsilon(t)}{\hbar}}\frac{d\epsilon(t)}{dt} = \langle\Phi_0^{\Lambda}|\hat{H}(t)e^{\hat{T}(t)}$$

We can replace the time derivatives of the amplitudes and the phase factor using the expressions derived above and then remove the phase factor exponentials from the equation

$$
\begin{aligned}
-\imath\hbar \sum_{j_\nu} \langle \Phi_0^{SCF}|{}^d\hat{h}_{j_\nu} \frac{d\lambda_{j_\nu}(t)}{dt} \\
&+ \sum_{j_\nu} \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] {}^e\hat{h}_{j_\nu} \langle \Phi_0^{SCF}|{}^d\hat{h}_{i_\mu} e^{-\hat{T}(t)} \hat{H}(t) e^{\hat{T}(t)} |\Phi_0^{SCF}\rangle \\
&+ \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] \langle \Phi_0^{SCF}| e^{-\hat{T}(t)} \hat{H}(t) e^{\hat{T}(t)} |\Phi_0^{SCF}\rangle \\
&= \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] e^{-\hat{T}(t)} \hat{H}(t) e^{\hat{T}(t)}
\end{aligned}
$$

Projecting from the right with an excited determinant, ${}^e\hat{h}_{i_\mu}|\Phi_0^{SCF}\rangle$, yields

$$
\begin{aligned}
-\imath\hbar \sum_{j_\nu} \langle \Phi_0^{SCF}|{}^d\hat{h}_{j_\nu} {}^e\hat{h}_{i_\mu} |\Phi_0^{SCF}\rangle \frac{d\lambda_{j_\nu}(t)}{dt} \\
&+ \sum_{j_\nu} \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] {}^e\hat{h}_{j_\nu} {}^e\hat{h}_{i_\mu} |\Phi_0^{SCF}\rangle \langle \Phi_0^{SCF}|{}^d\hat{h}_{j_\nu} e^{-\hat{T}(t)} \hat{H}(t) e^{\hat{T}(t)} |\Phi_0^{SCF}\rangle \\
&+ \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] {}^e\hat{h}_{i_\mu} |\Phi_0^{SCF}\rangle \langle \Phi^{SCF}| e^{-\hat{T}(t)} \hat{H}(t) e^{\hat{T}(t)} |\Phi_0^{SCF}\rangle \\
&+ = \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] e^{-\hat{T}(t)} \hat{H}(t) e^{\hat{T}(t)} {}^e\hat{h}_{i_\mu} |\Phi_0^{SCF}\rangle
\end{aligned}
$$

The matrix element in the first term on the left gives again $\delta_{i_\mu j_\nu}$, while the second term can be evaluate using the fact that excitation operators commute and so creating the resolution of the identity $1 - |\Phi_0^{SCF}\rangle\langle\Phi_0^{SCF}| = \sum_{j_\nu} {}^e\hat{h}_{j_\nu}|\Phi_0^{SCF}\rangle\langle\Phi_0^{SCF}|{}^d\hat{h}_{j_\nu}$, which gives then for the second term

$$
\begin{aligned}
\sum_{j_\nu} \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] {}^e\hat{h}_{j_\nu} {}^e\hat{h}_{i_\mu} |\Phi_0^{SCF}\rangle \langle \Phi_0^{SCF}|{}^d\hat{h}_{j_\nu} e^{-\hat{T}(t)} \hat{H}(t) |\Phi_0^{CC}(t)\rangle \\
&= \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] e^{-\hat{T}(t)} {}^e\hat{h}_{i_\mu} \hat{H}(t) e^{\hat{T}(t)} |\Phi_0^{SCF}\rangle \\
&\quad - \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] {}^e\hat{h}_{i_\mu} |\Phi_0^{SCF}\rangle \langle \Phi_0^{SCF}| e^{-\hat{T}(t)} \hat{H}(t) e^{\hat{T}(t)} |\Phi_0^{SCF}\rangle
\end{aligned}
$$

where the extra term on the right side here cancels the third term in the projected left-hand coupled cluster Schrödinger equation, which then reads

$$
\begin{aligned}
-\imath\hbar \frac{d\lambda_{i_\mu}(t)}{dt} + \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] e^{-\hat{T}(t)} {}^e\hat{h}_{i_\mu} \hat{H}(t) e^{\hat{T}(t)} |\Phi_0^{SCF}\rangle \\
= \langle \Phi_0^{SCF}| \left[1 + \hat{\Lambda}(t)\right] e^{-\hat{T}(t)} \hat{H}(t) e^{\hat{T}(t)} {}^e\hat{h}_{i_\mu} |\Phi_0^{SCF}\rangle
\end{aligned}
$$

This can be rearranged as the desired equation for the $\lambda_{i_\mu}(t)$ amplitudes

$$-\imath\hbar\frac{d\lambda_{i_\mu}(t)}{dt} = \langle\Phi_0^{SCF}|\left[1+\hat{\Lambda}(t)\right]e^{-\hat{T}(t)}[\hat{H}(t), {}^{e}\hat{h}_{i_\mu}]e^{\hat{T}(t)}|\Phi_0^{SCF}\rangle$$

11.9 The components of the coupled cluster vector function are given as

$$e_{i_\mu} = \langle\Phi_0^{SCF}|{}^{d}\hat{h}_{i_\mu}e^{-\hat{T}(t)}\hat{H}^{(0)}|\Phi_0^{CC}\rangle$$

The only thing in the above equation that depends on the cluster amplitudes is the cluster operator $\hat{T}$. Using the chain rule we get the derivative of the exponential operator as

$$\frac{\partial e^{\hat{T}(t)}}{\partial t_{j_\nu}} = e^{\hat{T}(t)}\frac{\partial\hat{T}}{\partial t_{j_\nu}} = e^{\hat{T}(t)}{}^{e}\hat{h}_{j_\nu}$$

Remembering that excitation operators commute, we can evaluate

$$\begin{aligned}\frac{\partial}{\partial t_{j_\nu}}e_{i_\mu} &= \langle\Phi_0^{SCF}|{}^{d}\hat{h}_{i_\mu}\frac{\partial e^{-\hat{T}(t)}}{\partial t_{j_\nu}}\hat{H}^{(0)}|\Phi_0^{CC}\rangle + \langle\Phi_0^{SCF}|{}^{d}\hat{h}_{i_\mu}e^{-\hat{T}(t)}\hat{H}^{(0)}\frac{\partial e^{\hat{T}(t)}}{\partial t_{j_\nu}}|\Phi_0^{SCF}\rangle\\ &= -\langle\Phi_0^{SCF}|{}^{d}\hat{h}_{i_\mu}e^{-\hat{T}(t)}{}^{e}\hat{h}_{j_\nu}\hat{H}^{(0)}|\Phi_0^{CC}\rangle + \langle\Phi_0^{SCF}|{}^{d}\hat{h}_{i_\mu}e^{-\hat{T}(t)}\hat{H}^{(0)}{}^{e}\hat{h}_{j_\nu}|\Phi_0^{CC}\rangle\end{aligned}$$

The two terms in the last line can be written more compact as commutator

$$\frac{\partial}{\partial t_{j_\nu}}e_{i_\mu} = \langle\Phi_0^{SCF}|{}^{d}\hat{h}_{i_\mu}e^{-\hat{T}(t)}[\hat{H}^{(0)}, {}^{e}\hat{h}_{j_\nu}]|\Phi_0^{CC}\rangle$$

which turns out to be an element of the coupled cluster Jacobian, A_{i_μ,j_ν}.